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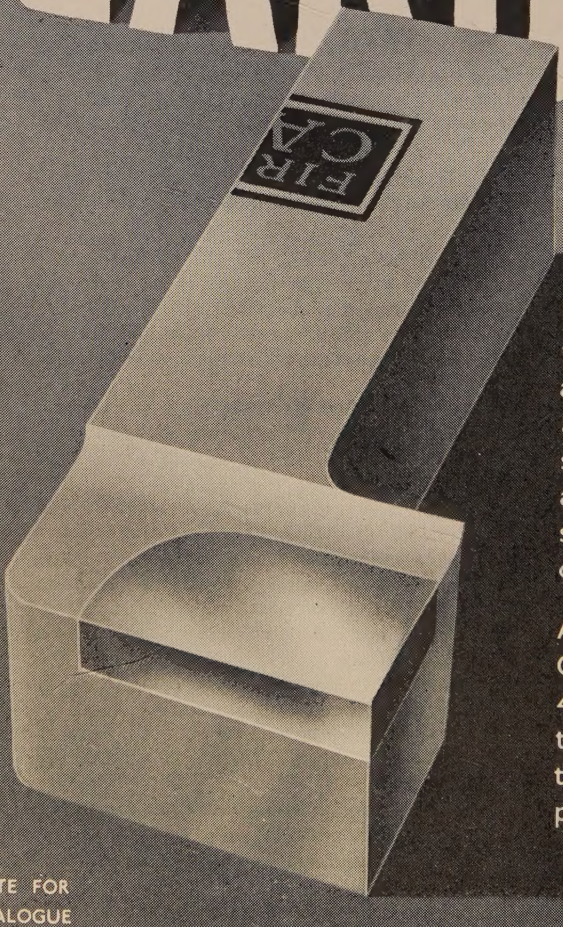

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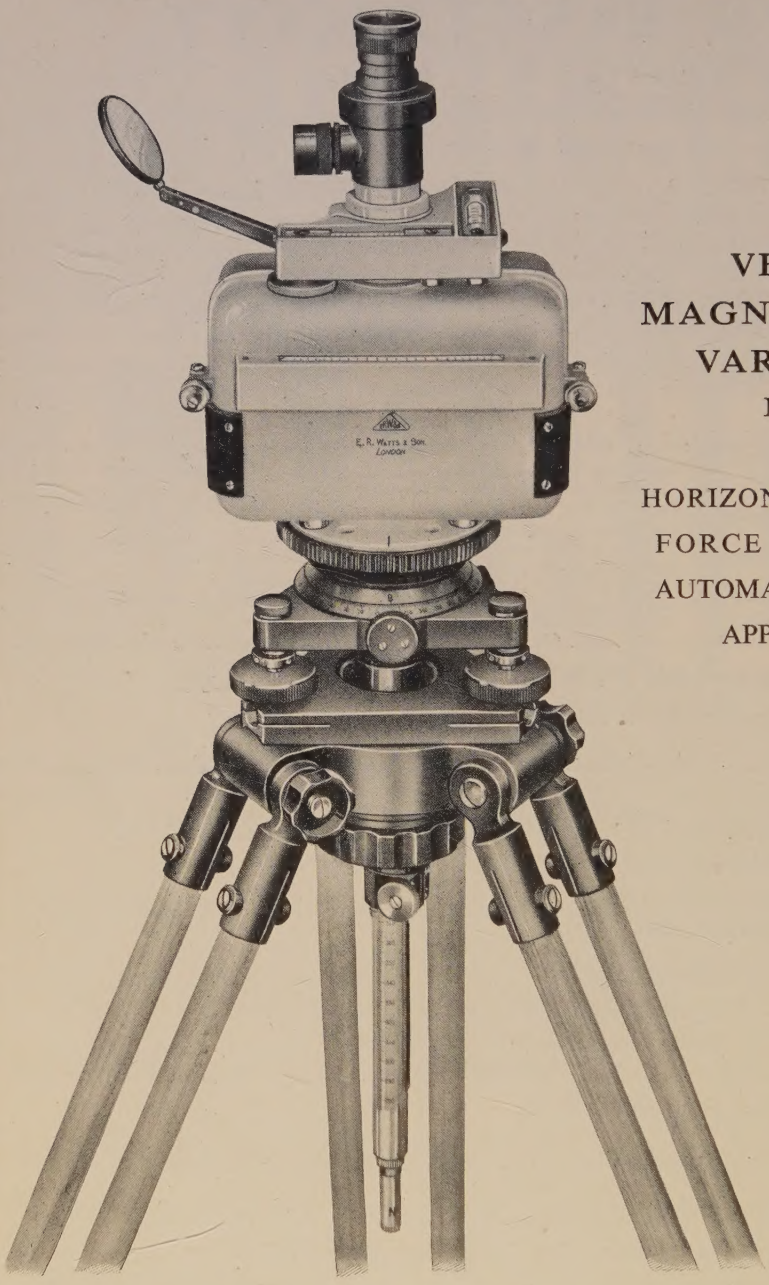

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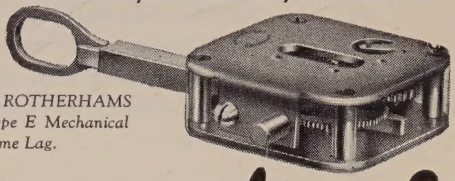

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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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I. SLIP IN SINGLE CRYSTALS

GLIDE AND HARDENING IN METAL SINGLE CRYSTALS

BY E. N. DA C. ANDRADE, F.R.S., London

ABSTRACT. A survey is made of recent experimental work on slip in single crystals of metal. Temperature has a great influence on the plastic properties, and the behaviour of different metals with the same crystal structure depends principally on the ratio of the temperature at which the experiment is conducted to the melting temperature of the metal. The experimental results are discussed in terms of the dislocation theory of slip.

SMEKAL made a valuable generalization when he pointed out that the properties of crystals could be divided into two classes: those, such as low-temperature ionic conductivity, which were largely influenced by small irregularities or impurities, and others which were largely independent of crystal individualities, that is, with which very consistent measurements could be obtained on unselected specimens. The former he called structure-sensitive, the latter structure-insensitive. The best way, perhaps, to approach the study of the mechanical properties of single crystals is with the realization that they offer one of the most striking examples of structure-sensitiveness known. A single crystal of copper at atmospheric temperature is very soft, a favourably oriented stress of 150 g.wt./mm.^{2} being sufficient to cause permanent set: after an extension of 50 per cent, its density, specific heat and such properties are practically unchanged, but its mechanical strength has increased by about 50 times. In some respects the crystal may be said to have roughly maintained its single crystal character, yet there is no doubt that there have been certain changes in the structure to which this surprising increase in strength is due. The lesson of this is that any theory of metal strength must concentrate on structural irregularities and neglect the properties of the regular crystal lattice.

A striking feature of the plastic deformation of metal single crystals is the preferential slip on certain crystallographic planes, and in each plane along a certain preferred crystallographic direction. Here again we meet at once with a feature

that emphasizes the inadequacy of any theory based on the ordinary conception of a perfect crystal lattice. On any such theory all parallel lattice planes are equivalent, but in practice slip takes place mainly on certain selected planes of a parallel system, giving rise to the well-known system of markings known as *glide bands* or *slip bands*. This means that there are certain minor structural differences between parallel lattice planes which lead to preferred slip on certain planes, or rather on certain very narrow assemblages of parallel planes, which may be called *glide lamellae*. The comparatively undeformed slab of crystal between two glide lamellae we call a *glide packet*. The thickness of such a glide packet varies widely according to conditions to which further reference will be made later, but is often of the order $5\,\mu$.

As regards the system to which the glide planes belong, conditions are simplest with crystals with a unique axis of symmetry, in particular hexagonal crystals. With these, slip takes place normally on the basic (0001) planes and in the direction of the digonal axis nearest to the direction in which the load is applied. There are, of course, three equivalent digonal axes, and when two of them are equally favourably inclined, glide may take place in short lengths alternately along the one and along the other, producing curious effects. The influence of temperature calls for reference, for Schmid has shown that at higher temperatures (above 225° C. say) glide may also take place on pyramidal faces $(10\bar{1}1)$ or $(10\bar{1}2)$. This is an indication that the glide planes cannot be explained simply in terms of the geometry of the lattice.

With crystals of cubic symmetry, the appearance is complicated by the fact that there are several sets of equivalent planes, as, for instance, the four octohedral (111) planes which act as glide planes with face-centred crystals. Here again temperature has an influence, for Boas and Schmid have shown that with aluminium above 450°, glide can also take place on cubic faces, i.e. (100) planes. The glide always takes place in a $[10\bar{1}]$ direction, which is the most closely packed direction.

With the face-centred cube, rhombohedral, hexagonal, and tetragonal crystal lattices, the glide takes place always in the direction of the most closely packed line in the lattice, and the plane on which the glide takes place normally is the most closely packed plane.

With the body-centred cubic system the position is peculiar. Whereas for each other crystal type a definite family of planes is given as the glide planes under ordinary conditions, to which another family may be added at higher temperatures, for this crystal type various planes have been found. For α-iron (110), (112) and (123) have all been given by different workers: for β-brass under certain conditions G. I. Taylor has given (110), while for tungsten at 20° C. Goucher has given (112). Mr L. C. Tsien, Miss Y. S. Chow and I have extended the search for the glide elements of body-centred cubic crystals to other metals—in particular to molybdenum, sodium and potassium—and other temperatures. We have found that (112), (110) and (123) are all possible glide planes and that temperature is the factor which determines which shall be operative. It appears that if T is the temperature (absolute) at which glide takes place and T_m the melting point, then the ratio

$\theta = T\ T_m$ governs the choice of the glide plane. The experimental results are summarized in the following table:

Metals	θ	Glide plane
W, Mo, Na	0·08–0·24	(112)
β-brass, Mo, Na	0·26–0·50	(110)
Na, K	0·80	(123)

Owing to the high symmetry of the body-centred system, the resolved shear-stress on the actual glide plane is seldom markedly smaller than that on the two other planes which come into operation at different temperatures. There seems, however, little doubt as to our results, while the rule suggested covers those of other observers as well. We have confirmed the influence of temperature by cutting a single long crystal of sodium into three parts, which were extended at temperatures in the three different ranges, and showed three different systems of slip bands.

In all cases the glide direction was the same, namely [111], which is the most densely packed line. The planes (110), (112), (123) belong to this zone axis. With α-iron Taylor and Elam[1] found that [111] was the glide direction, but that there was no true glide plane, the glide surface being, as it were, irregularly corrugated, with ridges and troughs parallel to [111]. Obviously this appearance would result if slipping took place simultaneously on narrow elements of (110), (112) and (123) planes bounded by lines parallel to [111] and intermixed with one another. The case of α-iron is particularly troublesome, there being little agreement among different workers. One difficulty is that of procuring even tolerably pure iron.

The general conclusion which I suggest may be drawn is that it is the glide direction which is fundamental, while the glide plane is determined by secondary considerations. Not only in the case of body-centred crystals, but also for the other crystals already quoted where temperature has an influence on the glide plane, the glide direction is fixed, and is the most densely packed line. Another indication that the glide planes are sensitive to minor disturbance is offered by some experiments of Greenland, who showed that, with the purest mercury, if the crystals are handled with the greatest care there are no true glide planes, but rather irregular surfaces reminiscent of Taylor and Elam's findings with α-iron, whereas if there is the slightest preliminary bending or twisting, the glide planes are perfect. It would appear as if the joining up of glide elements into a glide plane is determined by some minor factors involving purity, temperature and slight disturbances. In any case it is clear that the selection of glide planes is not to be explained by consideration of the geometry of perfect lattices.

It is well known as a fundamental fact that all metals give permanent yield at stresses far below, hundreds of times below, the theoretical strength, as far as this has any meaning. The qualification is inserted because on any theory based on the perfect lattice the behaviour should be quite different from what is observed: the crystal should show elastic behaviour up to a limiting stress, at which brittle fracture should occur. The elastic region with single crystals is actually extremely small, if it

exists at all: elastic strain certainly does not exceed an extension of 10^{-4}, and Chalmers[2] has found with tin at room temperature that creep occurs under the smallest stresses. The time element in the stress-strain curve is one of the great difficulties encountered in systematizing the experimental results.

One of the basic laws of crystal strength gives the criterion for yield, that the stress over the effective glide plane resolved in the glide direction shall have a certain value, the so-called critical shear stress. Closer examination shows, however, that what really happens, even under stresses less than those commonly accepted for this critical shear stress, is a very slow creep, although the rate of creep increases very rapidly when the stress exceeds a certain value. Roscoe and I[3] have shown, with cadmium at atmospheric temperature, that the rate u is given by a formula of the type

$$u = Ae^{-c(S-S_0)^2},$$

where S is a constant and S_0 is the resolved shear stress. This means that an arbitrary rate must be specified if S_0 is to have a definite value as the critical shear stress, and we have suggested 1 per cent per hour.

Impurities have a marked effect in increasing the critical shear stress; for instance the impurities in what is ordinarily called pure cadmium, viz. 0·11 per cent lead and 0·03 per cent zinc, cause the critical shear stress to be double that of spectroscopically pure cadmium, while mercury containing 1 part in 1000 of silver has a critical shear stress about four times that of the purest mercury, and 1 part in 1,000,000 gives a measurable effect. This is structure sensitivity with a vengeance. The impurities have a much smaller effect after the specimen has been heavily strained, which is significant. Some interesting experiments by Sachs and Weerts[4] deal with the critical shear stress of gold-silver alloys. They show a marked maximum at a composition of equal parts of the two metals, the critical shear stress being here about 5 times as great as that for either pure metal. No doubt the effect is comparatively small because the two atoms are so similar.

Temperature has a comparatively small effect on the critical shear stress. Meissner, Polanyi and Schmid[5] have measured this down to 20° absolute, with certain metals: with cadmium, for instance, the value at this temperature is only about 4 times what it is a few degrees below the melting point. Even at 1·2° absolute, where the critical shear stress was not measured, there is marked plastic yield. There are no signs that at absolute zero a crystal would behave as an ideal lattice should.

A characteristic of single crystals is the great hardening produced by strain, of which examples have already been quoted. At low temperatures, where the time effects are small, at any rate if the stresses are not very large, the conception of hardening is simple enough: under a given stress the strain reaches almost at once a tolerably constant value, and the stress-strain curve gives a measure of the strain hardening. At high temperatures, however, for large stresses there is a marked time creep, so that, even if the relevant strain is considered to be that attained within a very short interval of the application of the stress, there is an element of doubt.

Nevertheless, we can as a first approximation neglect the uncertainty caused by the time effect, especially if the time of loading is short, and obtain certain general results.

At low temperatures the strain hardening, as measured by the resolved shear stress at different increasing strains,* is particularly marked: for aluminium the resolved shear stress after 50 per cent extension at $-185°$ C. is about 6 times the critical shear stress for the unextended crystal, while at 300° C. it is not double. At low temperatures the form of the stress-strain curve is approximately parabolic, the stress increasing less rapidly than the strain. At higher temperatures the hardening is far less marked, and the law is nearer to a linear one. The effect of temperature is most marked in the middle region of temperature: at very low temperatures Meissner, Polanyi and Schmid have shown that, with cadmium, the hardening is practically independent of temperature, and at high temperatures the effect is not very pronounced. Nevertheless, the hardening, as measured roughly by the slope of the stress-strain curve, varies by a factor of 400 over the whole range. This is in strong contrast to the slight dependence of critical shear stress on temperature.

In connexion with the hardening it is doubtful if sufficient attention has been paid to the changes of structure that accompany it, as evidenced by x-ray analysis, although this has not been neglected by, for example, W. G. Burgers. Laue transmission photographs with an unstrained crystal show a series of spots of the size to be expected from the geometry of a perfect lattice: when the crystal has been strained, these spots are drawn out into the long smears known as asterisms. It has been shown by Burgers for aluminium and by Tsien and myself for sodium, for instance, that these asterisms, for all the spots, correspond to a rotation of crystallites about a line in the glide plane perpendicular to the glide direction.† It appears, then, that a severely strained crystal is no longer a single crystal.

Following up the idea that the rotations are intimately connected with hardening, Chow and I[6] have measured the spread of asterisms, with sodium, for equal extension (glide) at different temperatures. We find that at low temperature, where there is much hardening, the range of the rotations is markedly larger than at higher temperatures, where the hardening is less pronounced. This work is being continued.

The shear within the glide lamella itself may have a very high value (multiples of 10 if not multiples of 100), as may be seen at once when we remember that the displacement on such a lamella, of extremely small thickness, may be sufficient to lay bare, in the direction of slip, a strip of the plane whose breadth is of the order of 0·1 mm. The asterisms show that, within the range of rotations which they indicate, the original orientation is not strongly preferred. This may be interpreted to mean that rotation of crystallites does not take place in, or only in, the glide lamellae but in the glide packets. Whether the rotation is uniform within one glide

* It is best to work with crystals for which the glide plane lies near the axis of applied stress, so as to avoid geometrical softening effects.

† With sodium the asterisms consist of a row of discrete spots, which Chow and I have shown to be due to recrystallization.

packet, and varies from packet to packet, or whether each packet contains a range of angles, has not yet been established.

With the diminution of hardening as the temperature rises is connected, I think, another phenomenon which seems established, namely, that, generally speaking, the glide packets are thicker at high temperatures than at low. If we suppose that the hardening takes place through the agency of the glide lamellae, then if the hardening is considerable, glide will eventually stop in the lamellae on which it began, and start at intermediate places, the spacing between the lamellae thus becoming smaller and smaller, while if little hardening takes place on the initial lamellae it can continue on them. Roscoe and I found that with cadmium at atmospheric temperature, for which there is relatively little hardening and approximately a linear stress-strain relationship, at any rate within a limited region, the glide lamellae all appeared early, and increasing extension took place by further glide in these lamellae. With aluminium, on the other hand, where there is considerable hardening and a roughly parabolic stress-strain curve, Yamaguchi found that new lamellae continued to appear as strain progressed, the average distance between the planes being inversely as the stress.

This brief account makes no mention of many intriguing phenomena, especially that of twinning, which, in general, does not take place until there has been considerable strain hardening. It also omits all consideration of the mechanism of rupture, including brittle fracture, and of the effect of alternating stresses, to which Gough and his collaborators have devoted so much successful work. The purpose has been to emphasize certain general aspects, in particular the effect of temperature. Conclusions are too often drawn as to the behaviour of a particular metal from experiments at atmospheric temperature only, whereas, as I have earlier emphasized for polycrystalline metals, work over a wide range of temperatures tends to diminish the apparent divergencies of behaviour between different metals. As a rough first approximation—very rough—there would appear to be a law of corresponding temperatures, at any rate for metals of the same crystal lattice, the temperature of melting point giving the scale in each case.

The theoretical aspect of flow and hardening are to be discussed in detail by some of those chiefly responsible for our present knowledge in this direction, but a brief reference to the present position may be permitted.

The softness of the single crystals can be accounted for in a way originally suggested by A. A. Griffith to explain the mechanical behaviour of glass threads, by assuming that the solid contains flaws of some kind which produce a large local concentration of stress, in virtue of what may be called the "notch effect". The time flow can be generally explained by the conception of roughly periodic increases of stress due to local temperature fluctuations, as originally suggested by Becker. Orowan has combined these fundamental conceptions, and, by considering the critical shear stress as the stress sufficient to produce a fixed (very small) rate of flow, has explained the influence of temperature on the critical shear stress in a very satisfactory manner.

The theory of hardening, in spite of the great labour and ingenuity spent on

it, is not in a very satisfactory state. Experimental facts which seem essential, and which have not, perhaps, received full attention, are the glide lamellae and the crystalline rotations evidenced by the asterisms. The facts are simplest at very low temperatures, where the time element is not prominent and where, as has been pointed out, fresh glide lamellae appear throughout the hardening.* Here the hardening depends very little on temperature. This case is the one best adapted for the application of G. I. Taylor's purely formal theory, which gives the parabolic law experimentally found. Difficulties which the experimenter finds with the theory are how the dislocations arise, and, in particular, how and why their number should increase with the stress: further, the secondary system of flaws required to stop the propagation of the dislocations makes the machinery rather elaborate. The time element does not appear in the theory. These words do not indicate any lack of appreciation of this bold attempt to provide a quantitative basis for a theory of hardening.

The hardening at higher temperatures, where the influence of temperature is large, involves a consideration of the time element. Orowan has insisted that the rate of flow is the fundamental thing to be considered, as against the static conception which regards the stress-strain curve as giving the basic information. On this latter view the time flow is attributed to the recovery of the strained crystal elements. All flow can, of course, be considered as a relaxation phenomenon, so that the two conceptions are not, perhaps, fundamentally different, but the relaxation contemplated in the "static" view is a much slower process than that involved in the "dynamic" conception.

Orowan has pointed out that flow can take place at constant stress at the lowest temperature (1·2° absolute as shown by Meissner, Polanyi and Schmid), where the rate of crystal recovery is infinitely slow. This shows that flow can take place in the absence of recovery. At the same time, experiments by Dr Roscoe and myself show that with cadmium at high rates of extension and large extensions, there is both a recovery factor and a linear hardening such as is contemplated by Dr Orowan. The phenomena under the conditions just specified will probably require a more elaborate theory than may suffice for slow rates and small extensions.

Dr W. G. Burgers has put forward a theory which includes features suggested by Taylor, Orowan and Becker.

The fundamental difficulty, perhaps, is that which we meet with in trying to understand the polycrystalline metal—what takes place at the boundary between pieces of perfect lattice when the relative orientation is not consistent with a geometrical fit.

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* A generalization based, perhaps, on too little experimental evidence.

PROBLEMS OF PLASTIC GLIDING

By E. OROWAN, Birmingham

ABSTRACT: A discussion is given of the rate of flow in metal single crystals. Flow is believed to be due to the presence of dislocations; the rate of production and rate of movement of dislocations are treated.

§ 1. THE KINEMATICS AND DYNAMICS OF GLIDING

A FEW years ago the kinematics (crystallography) of plastic gliding was a self-contained domain that could be treated without paying much attention to dynamical questions. Recent researches, in particular those made by Prof. Andrade and his collaborators[1], have shown, however, that the operative glide plane and glide direction vary, in general, with the state of stress and with the temperature. Thus further progress in the crystallography of gliding has become largely dependent upon the development of our knowledge of its dynamics.

§ 2. THE SIGNIFICANCE OF THE STRESS-STRAIN CURVE

The development of the dynamics of gliding was, for many years, heavily impeded by a seemingly plausible, but actually wrong, hypothesis inherited from engineering mechanics. This hypothesis assumed that the plastic properties of materials can be described by stress-strain curves; in other words, that the dynamic law of gliding consists of a relationship between stress and strain. The empirical basis of this assumption (which we shall call the "static" hypothesis) was the following observation. If we apply a constant load to a commercial metal, the extension as a function of time will be given by a curve like figure 1*a*. There is, first, a period of rapid extension, lasting e.g. for a few seconds; after this the specimen has settled down to a comparatively constant length, and a period of very slow extension follows which, in general, lasts as long as the load is applied. Now the extension reached after the first period is plotted against the load in the stress-strain curve; the slow extension of the second period, the "creep", is made the subject of a special study independent of that of the stress-strain curve.

We see that the use of the stress-strain curve is an approximation permissible if the duration of loading is short enough to prevent appreciable creep, but longer than the first period of rapid extension. Thus stress-strain curves cannot be used for processes like rolling where the deformation takes place in a less time than the first period of extension.

When the study of the plasticity of metal single crystals began, the use of stress-strain curves was adopted without due realization of their roughly approximative nature, and for many years it was not noticed that this procedure does not even represent a rough approximation to the actual behaviour of single crystals. If we

apply a constant load to a single crystal, we obtain in many cases extension-time curves like figure 1*b*. This curve shows no sharp bend; it is impossible to determine without arbitrariness when the rapid extension ceases and when creep begins, and the crystal does not settle down to a more or less defined length. How was it, then, possible to obtain stress-strain curves at all? This was done in the following way. The extensometers used were so designed that the load increased continuously with time, and simultaneous readings of load and extension were used for plotting a stress-strain curve, without regard to whether the crystal would attain, at least approximately, a constant length under a constant load. It was not realized that any highly viscous Newtonian liquid, for example soft pitch or treacle, would give in this way stress-strain curves that are exactly like the typical stress-strain curves of metals, although there is no strain hardening, and no physical relationship whatever between stress and strain.

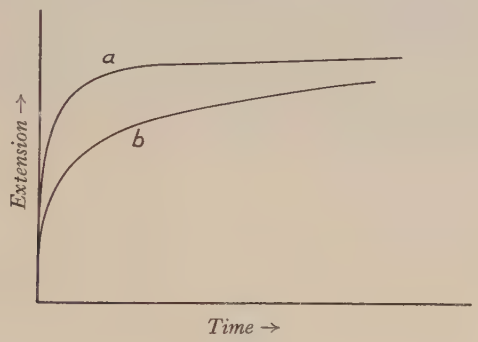


Figure 1.

It was well known, of course, that crystals "flow" under a constant load; this, however, was interpreted in the following way. It was assumed that, for any strain, the crystal would possess a certain "strength", represented by the corresponding ordinate of the stress-strain curve, and further deformation could take place only if the stress exceeded this strength. Plastic deformation produces internal distortions which make further deformation more difficult and thus increase the strength ("strain hardening"). The internal distortions produced by gliding are removed by thermal agitation: a strain-hardened crystal becomes soft again if it is kept for a sufficient time at a sufficiently high temperature. Now this "thermal softening" goes on during the extension test as well; consequently, if a constant load is applied to the crystal, plastic deformation will go on at such a rate that the thermal softening per unit time will just be compensated by the strain hardening produced by the deformation that takes place per unit time. Thus, according to the static hypothesis, any flow would be caused by thermal softening and no true flow would exist, that is, no flow independent of strain hardening and thermal softening.

However, it is easy to show that most observed cases of plastic flow certainly represent a true flow that cannot be explained by thermal softening[13, 15]. The time rate of softening decreases very rapidly with decreasing temperature. As an atomic

rearrangement process, activated by thermal agitation, softening shows the same typical temperature dependence as, for example, the velocity of chemical reactions, decreasing to about half or a third of its value if the temperature decreases by 10°. Now in the case of tungsten crystals the time constant of thermal softening reaches the value of one day probably at some temperature between 500° and 1000° C.; to be on the safe side, we assume that it is one day at 500° and that it is halved if the temperature decreases by 10°. The time constant at room temperature is then about a million million years; in other words, there is no thermal softening whatever at room temperature, and the whole amount of the abundant flow which tungsten crystals show at room temperature[2] is a true flow.

Another striking case is the flow of cadmium crystals at 1·2° K.[10]

The existence of a true flow shows that plastic gliding obeys a "dynamic" law; that is to say, the time rate of strain, not the strain itself, is a function of stress. The time rate of strain will depend, besides, on temperature and on the "state of strain hardening" of the crystal. The latter is not simply a function of the strain, but depends on all values which the strain and the temperature (and probably, the rate of strain) have had in the course of time.

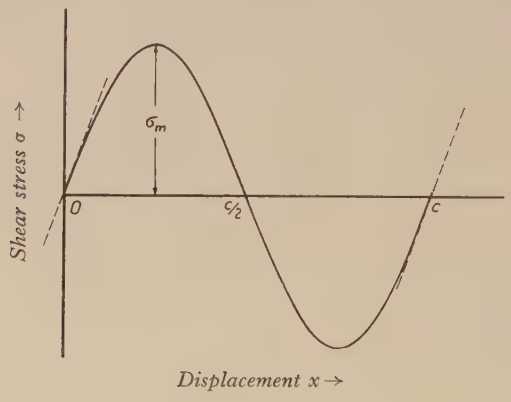


Figure 2.

§ 3. THE EXPERIMENTAL PROGRAMME

It would seem at first that the question whether true flow exists or not is rather an academic one. Actually, however, the answer to this question predetermines not only the programme of the measurements to be made but also the design of the extensometers to be used.

If there is no true flow, then

(*a*) the fundamental measurement to be made is that of the stress-strain curve; during this measurement

(*b*) thermal softening must be kept as small as possible; and

(*c*) the extension test must be continued until rupture occurs, in order to obtain the whole stress-strain curve.

(*d*) In the absence of thermal softening the rate of loading and its fluctuations are irrelevant; therefore any type of extensometer may be used.

(*e*) After finding the stress-strain curve, the effect of thermal softening is studied.

If true flow exists, on the other hand,

(*a*) the fundamental measurement is that of the rate of flow at different stresses and temperatures; during this measurement

(*b*) strain hardening must be kept as small as possible, and therefore

(*c*) the measurement must be made with extensions as small as possible.

(*d*) Extensometers must be used which allow the load to be kept constant and uninfluenced by the extension of the specimen and by inertia effects.

(*e*) After finding the rate of flow as a function of stress and temperature for the unhardened crystal, the effect of strain hardening can be studied.

This summary explains why, unfortunately, the majority of the dynamic measurements made under the influence of the static hypothesis (that is, the majority of the measurements made up to the present) are of little or no use; in fact, the main result from that period is that an explanation of plastic gliding on that basis is impossible, and an entirely new theoretical and experimental departure must be made.

§ 4. THE EXTENSOMETER

The first task is to design an extensometer suitable for the experimental programme set by the dynamic conception of gliding. The extensometers used so far belong partly to the "screw-and-spring" type in which one end of the specimen is pulled by a screw and the other connected with a spring which produces and at the same time measures the load, and partly to the weight-loading or to the electromagnetic type. In the first type, the spring contracts when the specimen extends, and therefore the load cannot be kept constant. In the second type, heavy masses are connected with the moving end of the specimen; owing to the jerky nature of extension in many important cases, the inertia of the masses produces large fluctuations of the load.

In the Physics Department of the University of Birmingham an extensometer has been built to suit the requirements of the new experimental programme. This is a weight-loading instrument in which between the weight and the specimen a soft spring is inserted; thus the load is independent of the extension, and at the same time inertia effects are practically eliminated by the spring. The extension can be interrupted after it has reached a previously adjustable amount, and it is photographically recorded with a low and a high magnification simultaneously.

It will be, of course, some time before a sufficient number of experimental results are available to allow us to draw a coherent picture of the plastic behaviour of crystals. In the meantime it is appropriate to put the question: What safe conclusions about the mechanism of plastic gliding can be drawn from the experience available at present? In what follows an attempt will be made to answer this question.

§ 5. THE DISCREPANCY BETWEEN THEORETICAL AND PRACTICAL STRENGTHS: DISLOCATIONS

The first fundamental problem of plastic gliding relates to the discrepancy between microscopic or "theoretical" and macroscopic strength[5, 17]. There is a simple and safe way to obtain an estimate of the maximum shear stress which the lattice can withstand. We choose a lattice plane as a glide plane, and in it a row of atoms as the direction of gliding. Let d be the distance between two neighbouring lattice planes of this sort, and c the distance between two atoms in the glide direction. If a shear stress σ acts in the glide plane parallel to the glide direction, two neighbouring planes suffer a relative displacement x; the shear strain is, then, x/d. For small values of x/d Hooke's law holds, and we have

$$\sigma = G.x/d, \qquad \text{.....(1)}$$

where G is the modulus of shear. In figure 2, where σ is plotted as a function of x, (1) is represented by the dotted straight line going through the origin.

If we assume that the distortion of the lattice remains strictly homogeneous, however large the strain, we see that for $x = c/2$ the stress σ must vanish, since all atoms of a plane are then symmetrically between two atoms of a neighbouring plane. For $x = c$ we have again the undistorted lattice, and the relationship between σ and x in the neighbourhood of $x = c$ is given by a straight line representing Hooke's law. Thus, obviously, σ must be approximately a sine function of x:

$$\sigma\sigma \simeq {}_m.\sin\frac{2\pi}{d}x, \qquad \text{.....(2)}$$

as shown in figure 2; σ_m is the maximum shear stress which the lattice can withstand; in other words, the microscopic or "theoretical" shear strength of the glide system considered.

For small values of x/c, (2) becomes approximately

$$\sigma \simeq \sigma_m.\frac{2\pi}{d}x; \qquad \text{.....(2a)}$$

this equation must be the same as (1), and comparing its constants with those in (1), we obtain

$$\sigma_m \simeq \frac{G}{2\pi}.c/d. \qquad \text{.....(3)}$$

c and d being, in general, nearly equal, we have

$$\sigma_m \simeq G/2\pi, \qquad \text{.....(3a)}$$

that is to say, the theoretical shear strength is approximately the modulus of shear, divided by 2π. This quantity is, for single crystals of the common metals, about 100 to 10,000 times greater than the actually observed macroscopic yield stress. What is the cause of this discrepancy?

First of all, there is discrepancy of the same magnitude between the microscopic and macroscopic tensile strength of brittle solids, like glass. This discrepancy has been explained by A. A. Griffith in a very satisfactory way which has been verified experimentally; it is caused by minute cracks or other defects, in the neighbourhood of which the local stress is much higher than the average stress in

the material. However, this explanation cannot be applied directly to plastic gliding. In the case of tensile strength, the stress concentration travels with the edge of the crack across the specimen when the crack begins to spread; if, however, the increased local shear stress at the edge of a crack starts gliding there, the edge of the crack remains where it was and does not cause a travelling stress concentration that would explain how the glide process is able to spread across the specimen.

It is easy to see, however, that a glide process, once started, itself creates the inhomogeneity necessary for its propagation. Suppose that a glide process started at P in figure 3 (figure 3*a* shows the glide plane, 3*b* its side view) and that, at some

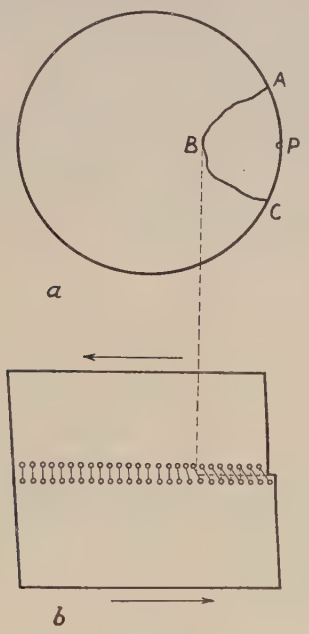


Figure 3.

moment, it has spread to the line ABC; in consequence, at this moment ABC separates those parts of the glide plane which have already undergone gliding from those which have not. The atoms of the lattice planes which glide upon each other are *still* in phase outside ABC and *again* in phase inside ABC. Along ABC, however, there is a zone in which the atoms of the lattice planes on both sides of the active glide plane are out of phase; they are more or less lifted out of the potential troughs of the field of the opposite lattice plane. Thus a relatively small stress will be sufficient to throw the atoms in this zone into their next equilibrium position and so to move the zone, that is, to propagate the glide process over the glide plane.

The zone of disorder along the line ABC has been termed by Prof. G. I. Taylor a *dislocation*. We shall call the line ABC (which can be a closed line if gliding has started from a point inside the crystal) a *dislocation line*, and the area inside this line the *dislocated area*.

It is important to realize that the existence of dislocations is not a hypothesis invented for explaining the discrepancy between microscopic and macroscopic strength. That dislocations *must* exist follows directly from the fact that gliding cannot take place simultaneously over the whole glide plane but must begin at one point and spread from there. In this connexion it is of interest that dislocations in the present sense were first treated by Prandtl in 1913[9, 20], long before the problem of macroscopic strength arose; he made use of them for a tentative theory of mechanical hysteresis. The above picture of the propagation of gliding over a glide plane was put forward by the author in his (unpublished) Thesis in 1929; the role of dislocations was independently recognized by others also, and the idea that gliding propagates over the glide plane by dislocations was introduced into the literature of plasticity in 1934 in simultaneous papers by Prof. Polanyi[18], Prof. G. I. Taylor[21] and the author[14].

The presence of flaws and dislocations shows that the crystal cannot possess the theoretical strength calculated for a homogeneous lattice. Whether dislocations actually lead to the observed values of the yield point is, of course, a separate problem. The critical stress necessary for setting a dislocation line into movement can be calculated if the width of the dislocation zone is known; this difficult mathematical problem has only very recently been solved by Prof. Peierls (cf. his paper later in this volume).

§ 6. THE EVIDENCE FOR DISLOCATIONS: THERMAL HARDENING

The conception that a perfect lattice has an extremely high strength and hardness and that the relative softness of real crystals is due to imperfections has often met with the following objection. Since plastic deformation creates imperfections and annealing removes them, it might be expected that crystals would become softer by plastic deformation and harder by annealing. According to common experience, however, the opposite is the case: deformation creates strain hardening which can be removed by annealing.

It is not difficult to recognize the cause of this seeming contradiction. The imperfections which cause the softness of the crystal are of the type of cracks or dislocations. The free energy of these imperfections is comparatively low, and a very thorough annealing is necessary to influence them. Furthermore, the softness of the crystal will not show any considerable change until the very last of these defects is removed or its efficiency diminished. On the other hand, the imperfections which cause strain hardening consist, according to x-ray evidence, of drastic distortions and rotations of the lattice; they are easily removed by annealing and to the extent that they are removed it is found that strain hardening diminishes. Thus, in general, only the hardening type of imperfections will be influenced by the usual kind of annealing, and, on the other hand, plastic deformation will not cause softening because, with most materials, softening imperfections are always present.

However plausible this explanation, it is very desirable that experimental evidence should be produced showing that the hardness of crystals can actually

be increased by removing imperfections, just as the tensile strength of glass[7], rock salt[8], and mica[11] could be considerably increased by eliminating surface defects. This experimental evidence was produced for zinc crystals[14]. A small extension in a spring-and-screw type extensometer, slightly exceeding the yield point, gave a stress-strain curve like curve 1 in figure 4; the load was then removed and the crystal given a rest of 24–48 hr. at room temperature (at which zinc crystals show comparatively rapid thermal softening). After this the crystals showed no trace of plastic deformation up to stresses far above the highest stress applied in the previous experiment—in one case, for example, up to a stress 30 per cent above

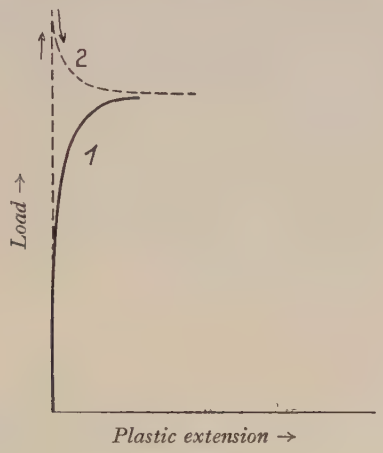


Figure 4.

the previously ascertained yield limit of the crystal. Frequently the crystal remained for many minutes under such high loads without any trace of extension; then a sudden dilatation occurred, the spring of the extensometer contracted, and the load fell until the crystal flowed slowly at the previously observed yield stress. This process is indicated by curve 2 in figure 4. Subsequent repetition of the experiment gave the first curve again: no sharp elastic limit could be observed and the crystal extended freely at its original yield point.

This experiment proves that the hardness of a crystal can increase by annealing and that it can suddenly decrease by plastic deformation. Consequently, the softness of real crystals can be attributed to imperfections and not to inherent structural characteristics of the lattice.

§ 7. THE EVIDENCE: STRAIN SOFTENING

An effect very similar to the "strain softening" and "thermal hardening" of zinc crystals is the well-known sudden yielding of soft steel; with the usual extensometers the stress drops after reaching the yield point (figure 5). It is still a subject of discussion among engineers how far this stress-strain curve is influenced by the design of the extensometer[19, 22]; as we have seen, the usual extensometers, as well as the usual methods of investigating the plasticity of metals, are essentially unsuitable for obtaining results with a physical meaning, since they are founded upon

the conception that no true flow exists. The practical justification of these methods is the intense strain hardening shown by most commercial metals; owing to this circumstance, the stress-strain curve obtained with a rapid extension is nearly independent of the rate of loading. This is not the case, however, for the initial stage of deformation of soft steel where the usual methods and conceptions lead to manifest contradictions.

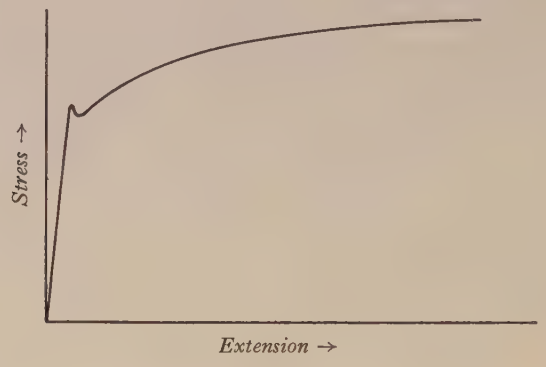
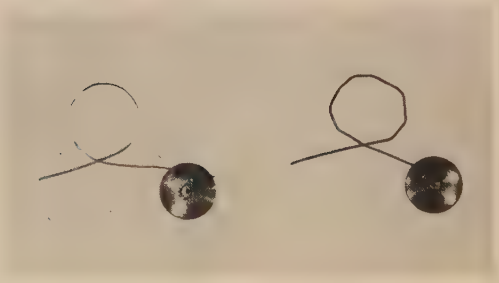


Figure 5.



Copper *Iron*

Figure 6.

We can easily prove, however, that plastic deformation actually makes annealed soft steel softer. If we bend a wire around a finger, the shape of the ring obtained will be different according to whether the wire hardens or softens by plastic deformation. If it hardens, bending will continue at those points where bending has not yet taken place and which, therefore, are still soft; the ring will be, then, of continuous curvature. If the wire is softened by deformation, bending will continue at the points where it began and which, therefore, have become softer; in this case the ring will be a polygon. Figure 6 shows that copper hardens and soft iron softens by bending. After the experience with zinc crystals there is scarcely any doubt that this strange behaviour of soft steel is due to the fact that the imperfections of the dislocation type are sensibly affected by annealing.

§ 8. THE PROPAGATION OF DISLOCATIONS

According to the previous considerations, plastic gliding involves two consecutive processes: the start of the glide process and its propagation. If one of these processes is much more difficult than the other, it alone will determine the velocity of plastic flow.

Let us assume that the amount a of glide in the glide process starting from the point P in figure 3 is one atomic distance in the glide direction.* After it has spread over the whole glide plane, the relative displacement of the two parts of the crystal separated by the active glide plane is a; in an intermediate stage the displacement is aZ/A, where Z is the dislocated area and A the area of the glide plane. The relative velocity of the two parts is $\frac{a}{A}\frac{dZ}{dt}$. The number of dislocation lines per unit length of the crystal, measured in a direction perpendicular to the glide plane, is NA, if N is their number per unit volume. Thus the rate of flow is

$$dx/dt = NA\,\frac{a}{A}\,\overline{dZ/dt} = Na\,\overline{dZ/dt}, \qquad \text{.....(4)}$$

where $\overline{dZ/dt}$ is the mean value of dZ/dt for all dislocation lines in the crystal.

In the special case when N is constant we have for the time average of the rate of flow

$$\overline{dx/dt} = Na\,\frac{1}{\tau}\int_0^\tau \frac{\overline{dZ}}{dt}\,dt = Na\,\frac{1}{\tau}\,A, \qquad \text{.....(5)}$$

if τ is the time in which a dislocation line spreads over the whole glide plane. Denoting by n the number of glide processes starting per unit time per unit length of the crystal (measured perpendicularly to the glide planes), we have

$$NA = n\tau, \qquad \text{.....(6)}$$

and from (5) we obtain

$$\overline{dx/dt} = na. \qquad \text{.....(7)}$$

Equation (7) can, of course, only be applied if the time τ of propagation, over which (5) is averaged, is much less than the duration of the extension test; only in this case is the rate of flow independent of the rate of movement of the dislocations and dependent only on the rate at which they are produced. The first attempts at a theory of plastic gliding actually assumed this to be the case; in other words, they assumed that the creation of dislocations is a process much slower than their propagation and, therefore, that it alone determines the rate of plastic flow. Subsequent experiments showed, however, that this is very far from being the truth. In these experiments [3] the jerky extension of zinc crystals was photographically recorded with high magnification and the start as well as the further development of the glide process was made directly perceptible. The recorded curves (such as figure 7) reveal two important things. First, that the glide process starts suddenly and gradually falls off; the average duration of vigorous flow is at room temperature

* If it amounts to two or more atomic distances, it can be considered as a superposition of two or more dislocations by one atomic distance each.

of the order of seconds; at 70° or 80° C. of fractions of a second; and at −10° or −20° C. of minutes. Secondly, that a single glide process, started obviously from one point of the crystal, produces gliding by thousands or even millions of atomic distances; in other words, a first impulse gives rise to a whole avalanche of dislocations. These are evidently not confined to a single glide plane, since the step-like glide markings upon the surface of the crystal are not sharp but rounded off[14, 6]; thus gliding in one glide plane can "infect" neighbouring glide planes, producing dislocations in them.

According to these experiments the conditions of equation (7) are not even approximately fulfilled, and the rate of flow must be calculated from the general

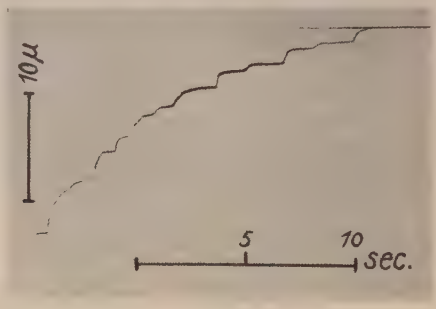


Figure 7.

equation (4). This represents a grave difficulty, since the rate of flow is given in (4) as a product of the number of dislocations per unit volume (or, roughly speaking, the number of active glide planes) and of the mean rate of increase $\overline{dZ/dt}$ of the dislocated areas, neither of which factors is directly observable. However serious this difficulty is, there is a hope that it can be surmounted by suitable experimental methods. If, in the course of an extension test, the stress is quickly altered by a small amount, the number of active glide planes will remain practically unaltered in many cases; whether this is so, can be checked by returning to the first stress again and seeing whether the rate of flow has its initial value. In this way the rate of propagation of the dislocations can be measured as a function of stress (and of temperature), and if this function is known, variations of N can be detected by using equation (4).

§ 9. THE ORIGIN OF DISLOCATIONS

The jerky extension of zinc crystals (which has also been observed with cadmium, rock salt, and other crystals) shows that gliding is more complicated than we might have assumed from consideration of the propagation of dislocations: the first glide step creates not one dislocation, but a large number of dislocations in different glide planes. This complication, however, is more than compensated by the opportunity given in the jerky extension of immediately perceiving the start of glide processes and thus being able to study the dependence of their frequency upon stress and temperature. This study could not previously be made, owing to the lack

of suitable extensometers; but it was observed that the frequency of the jumps increased very rapidly with the stress as well as with the temperature. It appears that the temperature dependence is of the same character as that of a chemical reaction. This behaviour is in striking agreement with a theoretical treatment given by Prof. R. Becker [2].

Let σ_m be the microscopic shear strength of the glide plane, σ the average stress and q the stress concentration factor at the point where gliding is to start; thus $q\sigma$ is the local stress there. A glide process will start before $q\sigma$ reaches the value σ_m, if a thermal fluctuation of stress raises $q\sigma$ to the value of σ_m in a sufficiently large volume. If A is the work necessary for this, then the probability of such a critical fluctuation will be, according to the theorem of Boltzmann, $p = Ce^{-A/kT}$. The work necessary for raising the microscopic shear stress $q\sigma$ to the value σ_m of the microscopic shear strength in a volume V is $A = (\sigma_m - q\sigma)^2 V/2G$, where G is the modulus of shear; thus the probability of a critical fluctuation is

$$p = C \exp\left[-\frac{(\sigma_m - q\sigma)^2 V}{2GkT}\right]. \qquad \text{.....(8)}$$

This formula gives a very steep increase of p with the stress and the temperature, as is shown by the jerky extension of zinc.

A somewhat puzzling feature of the Becker formula (8) is the volume V. The physical interpretation of this quantity is as follows. Suppose a glide process to start at the point P in figure 3, and the radius of the dislocation line to be r. The glide process is connected with a decrease of elastic energy, since the parts of the crystal adjoining the dislocated area have become free from stress; the decrease is proportional to the area and to the depth of the unstressed zone, which may be taken as proportional to r. Thus the change of elastic energy is $E_e = -Kr^3$. On the other hand, the dislocation zone represents an energy, consisting of an elastic part and of the mutual energy of atoms which are out of phase with respect to the opposite lattice plane. This energy E_d is proportional to the length of the dislocation line: $E_d = Lr$. The glide process will be stable if the change of energy for an infinitesimal change of r vanishes:

$$d(E_e + E_d)/dr = -3Kr^2 + L = 0, \qquad \text{.....(6)}$$

or

$$r = \sqrt{(L/3K)}.$$

The stress fluctuation must extend over an area r^2 of the glide plane, that is, over a volume $V \sim r^3$, in order to produce a stable dislocation; otherwise it is probable that the dislocation will not spread but vanish.

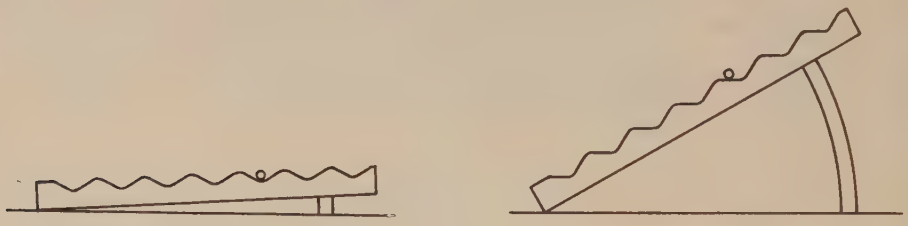
§ 10. THE RATE OF FLOW

The rate of glide flow will be determined, according to (4), by the number N of dislocations per unit volume and by their rate of propagation. The dislocations may be produced by critical stress fluctuations at stress concentrations; they may be present in the crystal from previous deformation or formed during the growth of the crystal.

As regards the propagation of dislocations, it is obvious that this process is connected with jumps across potential barriers, although these are much lower than the potential barriers of homogeneous gliding. Let σ_d be the average stress necessary to set a dislocation into movement in the absence of thermal movement. If the average stress σ is less than σ_d, the dislocation can still move with the help of thermal fluctuations; its velocity will be given by a formula of the type of (4), for example:

$$v = C \exp\left[-\frac{(\sigma_d - \sigma)^2 V}{2GkT}\right]. \qquad \ldots\ldots(10)$$

Here, however, we meet a problem which did not arise in the case of glide processes starting from stress concentrations. In a stress concentration, the shear stress $q\sigma$ certainly cannot exceed the microscopic shear strength σ_m; its highest possible value is σ_m, in which case gliding will start instantaneously, without having to wait for the help of a thermal fluctuation. A dislocation, however, will not run out of the crystal with infinite velocity if an average stress exceeding σ_d is applied; we must consider, therefore, the case when the average stress is higher



a *b*

Figure 8.

than the critical stress necessary for moving the dislocation without thermal help. In this case the mechanism of propagation will be quite different from that described by (10); the two mechanisms and the transition between them can be illustrated by a simple model.

Let the movement of a dislocation along a periodical potential field be schematically represented by the movement of a ball along a board with a wavy surface (figure 8), the ball being prevented by a guide from leaving the surface of the board. The application of a moderate stress is represented by a slight inclination of the board (figure 8*a*). The ball cannot leave a trough unless a thermal fluctuation throws it into the next. With the energy acquired the ball would be able to continue its movement without further thermal help if the board were rigid. Otherwise a part of its energy would be dissipated in the form of elastic waves and its movement would soon be arrested. Its mean velocity is proportional to the frequency of critical thermal fluctuations and is given, therefore, by a Boltzmann formula, with the value of the energy barrier between two troughs as A.

Now let the board be tilted until the potential barriers disappear (figure 8*b*). With increasing velocity the pulsating force exerted by the ball upon the board increases, and with it the energy of the elastic waves imparted at every step to the board. Finally the energy dissipated per step becomes equal to the potential difference

between two steps and then a stationary state is reached with a constant mean velocity which depends on the potential difference between two steps.

From the behaviour of this model we recognize that dislocations will have a well-defined velocity less than the velocity of sound even if the stress applied is higher than the critical stress σ_d necessary for moving dislocations without thermal help. This velocity is determined by a mechanism of momentum transfer between the gliding parts of the crystal; as the stress increases, the mechanism of the propagation of gliding will change over from the thermal activation mechanism expressed by (10) to this momentum transfer mechanism.

§ 11. VARIATION OF THE YIELD STRESS WITH TEMPERATURE

In the neighbourhood of the yield point the mechanism of the propagation of dislocations is probably a pure thermal activation mechanism. Whether the rate of plastic flow is mainly determined by the number of glide processes starting per unit time, or by the velocity of the dislocations, we may expect it to show the dependence upon stress and temperature expressed by the formulae (4) or (10).*

That the rate of flow increases very rapidly with stress is well known. That the equally rapid increase with temperature required by (4) or (10) actually exists was felt to be rather surprising at the time when the theory was put forward. In fact, the extremely steep temperature dependence following from (4) or (10) brought these formulae into discredit for many years; they were considered as refuted by the fact that metal crystals are plastic even at the lowest temperatures. This conclusion, however, was erroneous. By a relatively small increase of σ we can maintain the value of $(\sigma_m - q\sigma)^2/T$ and thus make the rate of flow invariant for any decrease of temperature.

From (4) or (10) a formula giving the variation of the yield stress with the temperature can be derived[12]. The yield stress is the stress at which the rate of flow reaches the limit Y beyond which it becomes easily observable. Thus using, for example, (10), the condition of yielding is

$$Y = \text{const.} = C \exp\left[-\frac{(\sigma_d - \sigma)^2 V}{2GkT}\right]. \qquad \ldots\ldots(11)$$

Assuming that V and G are approximately constant, we have

$$(\sigma_d - \sigma)^2/T = \text{const.} \qquad \ldots\ldots(11a)$$

or

$$\sigma = \sigma_d - B\sqrt{T}. \qquad \ldots\ldots(12)$$

The experimental results agree very well with this formula which, at present, is the only theoretical result relating to the dynamics of gliding that can be tested quantitatively by the measurements available.

* For very small stresses (4) or (10) obviously cannot give the rate of flow; it is easy, however, to give a generalized formula which applies in this case also[16].

§ 12. THEORETICAL SIGNIFICANCE OF THE YIELD STRESS

The assumption made in deriving (12), that V is nearly constant, requires some explanation. If the process that determines the rate of flow is the creation of dislocations at stress concentrations, then K in (9), and thus V, will depend on the stress. If, on the other hand, the rate of flow is mainly determined by the velocity of dislocations, then the linear dimensions of V may be determined by the thickness of the dislocation zone and they may be more or less independent of σ. The success of formula (12) indicates that the yield point is the stress at which the dislocations begin to be mobile, not the stress at which the number of glide processes started at stress concentrations begin to increase rapidly.

This conclusion is supported by other observations. First, the experiments mentioned show that a zinc crystal, hardened by the removal of effective dislocations and flaws, regains its usual mode of yielding and its usual yield point after plastic deformation has taken place, i.e. after dislocations have been produced. Second, it is well known that the yield point cannot be influenced like the tensile strength of brittle materials by altering the state of the surface. All this points to the conclusion that the yield stress is the stress at which the dislocations become mobile, or capable of producing avalanches of new dislocations, in the sense of § 8.

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GEOMETRICAL CONSIDERATIONS CONCERNING THE STRUCTURAL IRREGULARITIES TO BE ASSUMED IN A CRYSTAL

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ABSTRACT. Various workers have assumed that slip in a metal is propagated by the motion of dislocations through the lattice. The geometrical and mechanical properties of some types of dislocation have been investigated. It is shown that plane systems of simple dislocations can break up a crystal into crystallites of the kind discussed by Bragg[8].

§ 1. INTRODUCTION

A point which is brought out by discussions concerning internal strains and deformation properties of crystalline substances is the need for a well-defined picture of the types of irregularity to be found in the interior of a crystal. It would appear that an investigation of the geometry of dislocations can be of great help in this respect, and the following notes may serve to show this.

The term *dislocation* is often used in various connexions without further specification; the application of this term to denote a particular elementary type of deviation from the ideal lattice structure is due to Orowan[1,4], Polanyi[2] and Taylor[3]. Taylor has given a precise picture of the simplest two-dimensional case. Taylor's case, however, needs generalization (Orowan had already considered a more general type). This generalization has been the subject of a recent communication by the present author[5], the main points of which will be summarized here, together with some further developments which enable us to complete the picture in several respects.

The lattice to which the considerations will refer is of the simple cubic type. This restriction is introduced in order to bring forward the basic points of the analysis as clearly as possible, and to avoid the complications which arise when face-centred or body-centred lattices, non-regular lattices, or lattices containing atoms of more than one kind, are to be investigated. The possibility, however, must be kept in mind that dislocations in more complicated lattices may show properties which are of importance for the behaviour of a crystal during deformation, but which are not found in the present model.

In order to specify directions, rectangular coordinates x, y, z will be used, with the axes parallel to the principal directions of the cubic axes of the lattice.

§ 2. DISLOCATIONS OF THE EDGE TYPE

The simplest type of dislocation is obtained when it is imagined that in an originally perfect lattice a cut is made over a certain area of a plane perpendicular, say, to the x axis, and that along this cut either a layer of atoms is removed from the lattice, or an extra layer of atoms is introduced into it. When the cross dimensions

of the area are large compared with the atomic distance λ_0 (e.g. more than 10 or 20 times this distance), it can be assumed that the lattice in the neighbourhood of the cut will contract (in the first case; see figure 1) or expand (in the second case) in such a way that over the central part of the area of the cut the arrangement of

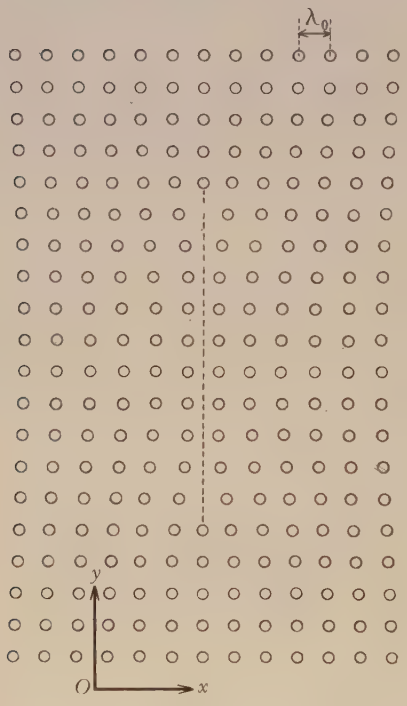

Fig. 1.

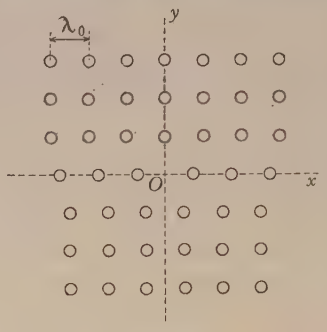

Fig. 2.

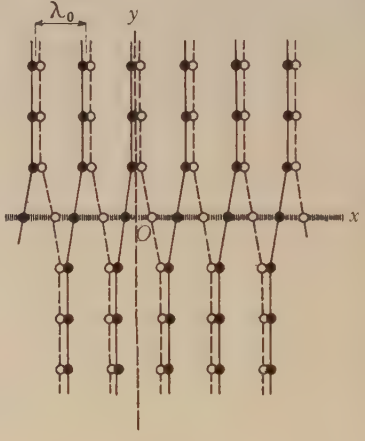

Fig. 3.

Figure 1. Sketch of a dislocation obtained by removing the atoms over a certain area of a lattice plane perpendicular to the x axis. (The displacements of the atoms in the y direction have been neglected in the diagram.)

Figure 2. Elementary two-dimensional dislocation, having the z axis (perpendicular to the plane of the paper) as its edge line.

Figure 3. Schematical picture of a dislocation line of screw type, lying along the x axis. Continuous lines indicate rows of atoms above the x, y plane; broken lines indicate rows of atoms below this plane.

the atoms will have reassumed the original regular cubic type, while deviations will be found only in the neighbourhood of the contour of the area. When the area over which the cut has been made and, e.g., an extra layer of atoms introduced is the half plane $x=0$, $y>0$, we obtain the situation roughly sketched in figure 2, which brings us back to Taylor's case.

Considering the displacements u, v, w of the atoms from their original positions, it will be seen that, in the case of figure 2, for atoms to the right of the cut (and not

too near the edge) we have $u = +\lambda_0/2$, whereas for atoms to the left of the cut we have $u = -\lambda_0/2$. There is thus a discontinuity in the course of u (considered as a function of x, y, z) when we pass through the area of the cut; no such discontinuity exists for the components v, w. For mathematical purposes it is useful to assume, instead of considering u as given by a discontinuous function, that u is described by a continuous but multi-valued function, with the cyclic constant λ_0 for every line which embraces the edge of the cut. The dislocation is fully determined by giving the contour of the area over which the cut has been made and the value of the cyclic constant associated with the displacement component u. The contour of the area mentioned will be called the *dislocation line*, and it is to be observed that in the cases considered, the dislocation line is situated wholly in a plane perpendicular to the direction of the displacement component which suffers a discontinuity. Such dislocation lines will be said to be of the *edge* type.

§ 3. DISLOCATIONS OF THE SCREW TYPE

It is possible also to consider dislocations characterized by a dislocation line *parallel* to the direction of the displacement component which suffers the discontinuity. That such cases should be introduced will be evident e.g. from the case pictured by Orowan in figure 3 of his paper. The nature of the deviation from the normal lattice arrangement in the neighbourhood of such a dislocation line is indicated schematically in figure 3. It can be imagined to have been obtained, e.g. by cutting the lattice along the half plane $y = 0$, $z > 0$, and making a shift of one atomic distance in joining together again the quarter planes $x = \text{const.}$, $y < 0$, $z > 0$, and the quarter planes $x = \text{const.}$, $y > 0$, $z > 0$. In this case it is again the displacement component u which shows a singularity; it increases (or decreases) by the amount λ_0 when a closed curve is described surrounding the x axis. Dislocation lines of this character will be said to be of the *screw* type.

Cases of a more general nature can be constructed by joining segments of dislocation lines of both types, and it will be evident that (considered on a scale large compared with atomic distances) lines of arbitrary spatial form can be obtained. An important property of these lines must be noticed: like vortex lines in a fluid, they can never end at an interior point of the substance; consequently they must either be closed in themselves, or extend towards boundary surfaces of the lattice or to infinity.

§ 4. STRESSES IN A DISLOCATION

Although the exact positions of the atoms in the neighbourhood of the dislocation line will depend upon the atomic forces, etc., a fair approximation can be obtained by applying the equations of the theory of elasticity. The basic formulae have been given by Volterra for the case in which the equations of the isotropic elastic body are used; their application to the present subject is indicated in the communication mentioned before[5], in which also the extension to the case of the non-isotropic substance of regular symmetry has been worked out. The formulae

obtained describe the course of the displacement components u, v, w as functions of the coordinates x, y, z, and further make it possible to find the values of the mean elastic stresses per unit area in the medium. As the atoms along the dislocation line are not subjected to special external forces, the distribution of the elastic stresses must be such that when a small cylindrical element of the medium with its axis along an element of the dislocation line is considered, the stresses acting upon the cylindrical surface (which stresses are of an order of magnitude inversely proportional to the radius of the cylinder) must balance each other.*

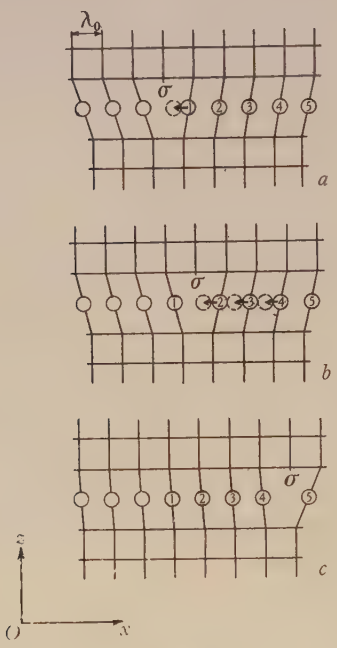

Fig. 4.

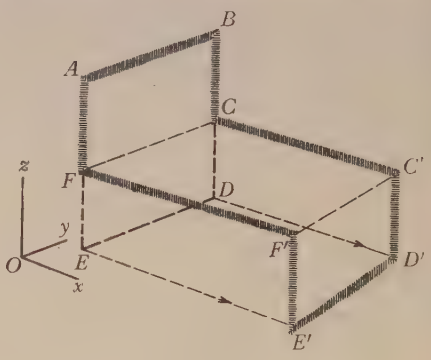

Fig. 5.

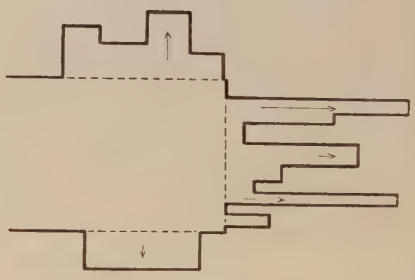

Fig. 6.

Figure 4. Schematic picture of the migration of a dislocation line of edge type through a lattice.
Figure 5. Schematic picture of the migration of a part of a dislocation line, whose original form was *AEDC*, causing the appearance of dislocation lines of screw type *FF'* and *CC'*.
Figure 6. Sketch of an irregular migration of a dislocation line.

§ 5. MOTION OF DISLOCATIONS

The next point to be considered is the *migration* of a dislocation through a lattice. The passage of a single two-dimensional dislocation line of the *edge* type through an otherwise undisturbed lattice has been described by Taylor; a schematic picture is given in figure 4. Such a migration of a dislocation line across a lattice is accompanied by a relative shift of the two parts into which the lattice is divided by the plane (sufficiently prolonged) described by the migrating line,

* From the results obtained for the displacement of the atoms by means of the formulae mentioned, it would appear that the dislocations are to be considered as "short dislocations" in the terminology used by Peierls (this volume).

provided the lattice is not of infinite extent. When A is the area described by the line and A_0 the area of the cross-section of the lattice by the plane over which the dislocation line has moved, the magnitude of this relative shift is given by $\lambda_0 A/A_0$.

When instead of an infinitely extended straight dislocation line we have a closed line of the edge type, it is necessary to assume that the various segments of the line can move independently of each other. If this were not the case, the migrating line would always remain in a single plane, being displaced parallel to itself, and there would be no relative shift between the parts of the lattice lying outside the cylindrical surface described by the migrating line. A simple case in which one part of the line moves independently of the rest has been indicated schematically in figure 5, where it has been assumed that the part $FEDC$ of the dislocation line has moved parallel to itself to the position $F'E'D'C'$. The tracks FF' and CC' described by the end-points then become dislocation lines of screw type. If A denotes the area $FF'C'C$, the same formula holds for the relative shift of the parts of the lattice as before.

The case of the growth of a dislocation line considered by Orowan in figure 3 of his paper[4], where a line originally of very small extent increases the area enclosed by it in all directions, shows that we must also assume that a dislocation line of screw type can migrate in a direction perpendicular to itself.

It is possible, perhaps, that when several segments of a dislocation line move forward, segments between them remain at rest, so that the line might assume a form of the kind pictured in figure 6.

§ 6. INFLUENCE OF INTERNAL STRESSES

The dynamics of the migration thus far have been investigated only for lines of the edge type[3,6]. The atoms lying along the dislocation line find themselves in potential troughs of much smaller depth than normally is the case, and there exists a definite probability that heat motions may throw these atoms into neighbouring equilibrium positions, as has been sketched in figure 4. Whereas the heat motions in an unstressed lattice will have no preference for a displacement to or fro, a difference will arise when a suitable exterior shearing stress is acting upon the lattice: in such a case there will be a preference for jumps in such a direction that the resulting relative shift of the parts of the lattice is in accordance with this shearing stress.

The mechanism of the migration of a dislocation line of screw type in a direction perpendicular to itself has not yet been analysed.

It must be noted that every dislocation line has a field of stress around itself. When a dislocation line has been displaced and has changed its form under the action of an exterior shear stress, the shear stress due to the field of stress of the line itself must also be taken into account. This field can be such that it will counteract the exterior stress at certain regions of the lattice, and it is possible that when the exterior stress ceases to act, the self-induced stresses will tend to annihilate certain details of the change of form which the line had suffered.* It may be sup-

* Some cases have been considered by Burgers on p. 315 of reference (5).

posed that a dislocation line will be in equilibrium under its own field, only when it lies wholly in a plane perpendicular to the displacement component which is discontinuous, so that all segments of screw type will have disappeared.

§ 7. SYSTEMS OF DISLOCATIONS

We now pass on to systems of dislocation lines. It might be imagined that the structural irregularity to be assumed in a natural single crystal would be due to the presence of a great number of dislocation lines, arbitrarily distributed over the lattice. From what we have seen above concerning the migratory properties of dislocation lines it would follow that the crystal would in that case show slip when it is subjected to a shearing stress, and shear hardening might perhaps be explained (*a*) as a consequence of the self-induced stresses (the interior field) of the deformed dislocation lines, or (*b*) by assuming that dislocation lines come near to each other or cross, and that such happenings may impede the process of migration. The picture obtained in this way is, however, unsatisfactory in a number of respects: (1) it is too indefinite; (2) without a detailed investigation we cannot rely upon the validity of the assumptions (*a*) and (*b*) above; and (3) the deformation of the dislocation lines caused by the application of an exterior stress might vanish in consequence of the action of the self-induced stresses as soon as the exterior stress ceased to act, and then the crystal would slip back; (4) the large local slips observed along slip planes in many cases[7] would require the presence in a small space of a number of dislocation lines much greater than could be introduced with ease into the lattice.

The remedy for the latter points appears to be the assumption that in the process of slip an important part is played by dislocations formed afresh at suitable spots at the surface of the crystal.

With regards to the lack of definiteness in the picture, this can be removed by making use of the assumption of a mosaic pattern of the type described by W. L. Bragg[8]. The picture developed by Bragg can indeed be made more precise by assuming that the boundary surfaces between the differently oriented domains of the mosaic which make up the single crystal are formed by sets of parallel dislocation lines.

An example is given in figure 7. Here two domains are shown, separated by a set of parallel dislocation lines of edge type regularly spaced with the period h (equal to some multiple of λ_0) over the plane Oyz (perpendicular to the displacement component u which is discontinuous at the dislocations). The two domains are free from stress at distances from the transition surface which are large compared with h; they are inclined with respect to the plane Oyz over angles $\frac{1}{2}\lambda_0/h$, and make an angle λ_0/h with each other.

In this case the transition surface has the direction of a lattice plane. Transition surfaces making an arbitrary angle with the lattice planes can be built up from a double set of dislocation lines of edge type, one set introducing discontinuities into u and the other set into v.

A case of different character is obtained by assuming a set of dislocation lines of screw type, say all parallel to the axis Ox, lying at equal distances h in the plane Oxy. The configurations of the rows of atoms just to the positive and just to the negative sides of this plane are then of the types sketched roughly in figure 8. At

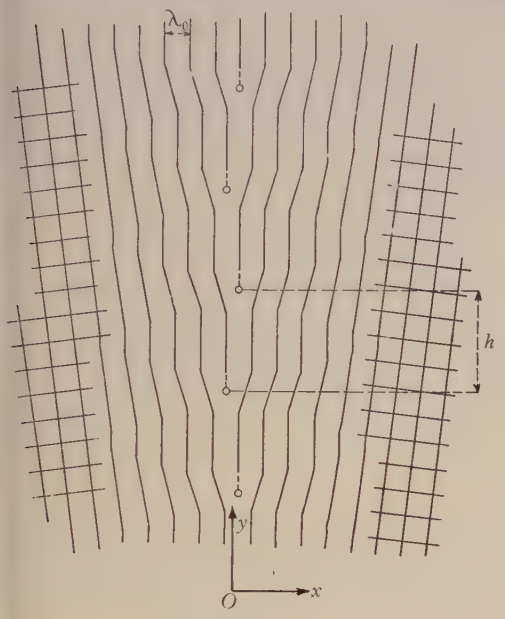

Fig. 7.

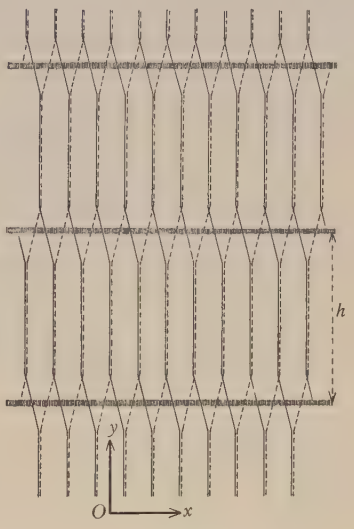

Fig. 8.

Figure 7. Schematic picture of a transition surface between two domains, formed by a set of parallel dislocation lines of edge type, all situated in the plane $x=0$.

Figure 8. Schematic picture of a transition surface between two domains, formed by a set of parallel dislocation lines of screw type. Continuous lines indicate rows of atoms immediately above the plane of the paper; broken lines indicate rows of atoms immediately below this plane.

larger distances these rows become straight again, but then they are inclined with respect to the y axis through angles $\pm \frac{1}{2}\lambda_0/h$, so that the two domains appear to be rotated relatively to each other through the angle λ_0/h.*

It is to be expected that by suitable combinations of such cases all necessary positions of transition surfaces can be obtained, and it is to be noted that in this way we have ensured the best possible fit between the mutually inclined domains.

* The case of figure 7 has been treated by the author[5]. The case of a double set of dislocation lines can be constructed upon similar principles; it is to be observed that a certain relation must be fulfilled between the spacings of the two sets and the angle of inclination of the transition plane, in order that at great distances from this plane the lattices shall be free from stress. A third case—set of parallel dislocation lines of screw type—would at first sight seem to present a difficulty or an indeterminateness. It is to be observed, however, that the assumption of a set of infinite lines is an impossible abstraction; actually the dislocation lines are situated on the transition surfaces between the domains, and as they cannot end in the interior of the lattice, a more suitable picture is obtained by combining various sets, so that e.g. a set of lines of screw type at each end is united to a set of lines of edge type, and so on. A domain having the form of a rectangular prism embedded in a larger mass, for instance, may be imagined to be surrounded by a set of closed rectangular dislocation lines, lying at regular spacings one above the other.

This will be seen in particular when the angles between the domains are small, say of the order of half a degree or less (as will be the case in natural crystals, which have not been subjected to cold working), for the spacing h of the dislocation lines will then be of the order of $100\lambda_0$ or more. In such cases there are large areas of the transition surfaces where the arrangement of the atoms is practically normal; in this way all the domains belonging to the same crystal form one coherent complex, and there are no amorphous transition layers. The transition surfaces moreover possess the mobility required by Bragg. Finally, when the domains themselves have dimensions of the order 10^{-4} cm., equal to about 10,000 λ_0, the interior region of each domain will be practically free from stress.

§ 8. THE MECHANISM OF PERMANENT DEFORMATION

What now will happen when such a mosaic-patterned single crystal is subjected to an exterior shear stress? In the first place there will appear an elastic deformation, and at the same time some shifts of the transition surfaces may occur. So long as these are small, they will probably be more or less reversible, though every motion will be accompanied by some dissipation of energy, so that a certain internal friction will appear. This supposition fits in with the remarks made by Zener at the end of § 3 of his paper[9].

The displacement of the transition surface between two adjacent domains will lead to a change of position (a rotation) of the region traversed by the transition surface, as this region shifts its allegiance from one domain to the other. This rotation, however, will be only of small amount, and it does not introduce a new direction into the mosaic.

It is to be expected, nevertheless, that these shifts of transition surfaces and these rotations, in consequence of the circumstance that we have to do with a three-dimensional arrangement, will produce stresses in the lattice not present before. It consequently seems logical to suppose that the shifts can be of limited amount only.*

Hence, as has been mentioned already, in order to account for large amounts of slip, another phenomenon must be assumed, and when the exterior shear stress is sufficiently large we must expect that new dislocation lines will penetrate into the crystal, originating from suitable spots on the outer surface, as has been suggested, e.g. by Orowan[4]. The experimental observations on the formation of slip bands suggest that these new dislocation lines can move through the crystal over large distances; hence we must suppose that their migration is not greatly hindered by the transition surfaces between the various domains of the mosaic. The picture developed in the preceding section is not in contradiction with such a supposition,

* Plastic deformation in consequence of a displacement of the existing transition surfaces may perhaps also be the process underlying the microplasticity observed in tin by B. Chalmers[10]. In a contribution to the *Second Report on Viscosity and Plasticity* (Amsterdam, 1938), p. 215, the idea had been expressed that this microplasticity was due to individual jumps of the atoms of a type not further specified; it had been supposed there that it would lead to a velocity of creep dependent, at a given temperature, only upon the shear stress. The present picture affords the possibility that the velocity of creep will decrease, perhaps to zero, with increasing displacement of the transition surfaces; such a decrease was actually observed by Chalmers.

as the angles between the domains are small and the domains fit together very nicely over large areas of the transition surfaces. As the direction of a dislocation line, however, is connected with the directions of the lattice in which it finds itself, it follows that the dislocation lines when moving through the mosaic-patterned crystal will not remain straight, but will consist of segments making small angles with each other.

It seems logical to suppose that the motion of these new dislocation lines across the mosaic of differently oriented domains will not go back (at any rate not farther than the side of a domain) when the exterior stress ceases to act.

The new dislocation lines will probably be formed at those spots on the exterior surface of the crystal where transition surfaces between domains meet this surface and where there is a possibility of the latter surface possessing re-entrant angles, since at such places concentration of stresses will occur. We must expect that at suitable places dislocation lines will be formed repeatedly, and will then travel through the crystal approximately, or perhaps exactly, along the same path. In this way slip bands will be formed, and it is conceivable that the amount of slip along such a band may become very large. At the same time we may expect that when a large number of slip bands is formed in a crystal, the distances between them will be of the same order as the dimensions of the domains.

§ 9. STOPPED DISLOCATIONS

The most important and at the same time the most difficult problem is to develop a picture of the dynamical relations involved in the process. The motion of a dislocation line through the mosaic of differently oriented domains will require greater forces than the motion through an ideal lattice for, at every transition, local surface stresses must be overcome. It is not improbable that these local stresses and the irregularities in the atomic arrangement at the spots where a new dislocation line crosses already existing lines will lead to irregularities in the migration of the new line, and perhaps may stop its motion at certain places. The passage of a new dislocation line through a domain causes a relative shift of the two regions into which the domain is separated by the plane over which the line moves; should many lines move along the same path, then this relative shift will become considerable, and may bring about the appearance of large interior stresses. It is conceivable, therefore, that in certain cases the first dislocation lines of a slip band may travel across the whole crystal, while afterwards, when certain shifts have taken place in the domains traversed, lines travelling along the same track may be stopped.

When a dislocation line is stopped somewhere, it will remain in the lattice as a permanent distortion, and it is evident that when a number of dislocation lines travelling approximately along the same track are stopped at approximately the same place, a large local deformation of the crystal will appear at this place. As dislocation lines will penetrate into the lattice from both sides, it is possible that the local deformation, which has arisen from stopped dislocations coimng from one side, may next cause the stopping of dislocations coming from the opposite side.

It would be necessary to make an analysis of the various cases which may present themselves in consequence of such processes. We have attempted to give a sketch of a simple case in figure 9, where AA' represents the track (glide plane) for a group of dislocations which originated on the left-hand side of the crystal and were stopped in the neighbourhood of A', while BB' represents the track of a similar group coming from the right-hand side, stopped in the neighbourhood of B'. For convenience only one dislocation of each group has been pictured; to indicate further details would lead to complications, and it is possible that the various stopped dislocation lines influence each other in some definite way. Moreover, the

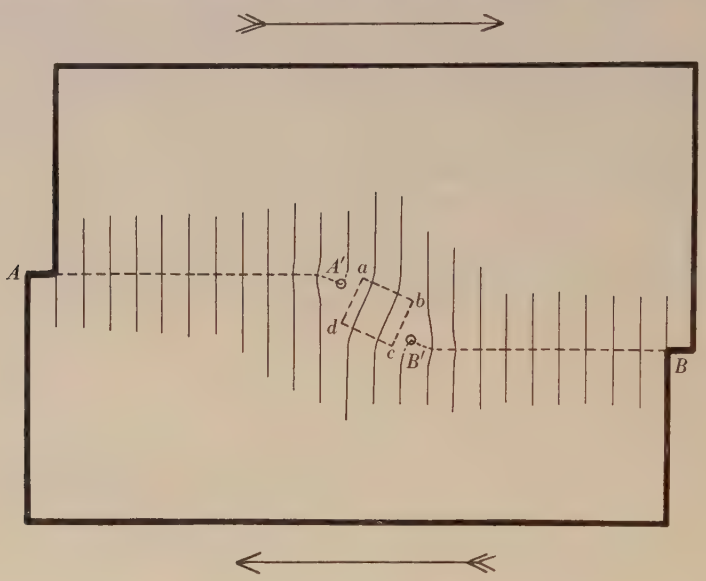

Figure 9. Schematic picture of a crystal subjected to shear. The mosaic structure has not been indicated. AA', BB', tracks of two groups of dislocations which have been stopped at A' and B' respectively.

original cause of the stopping is to be sought in the details of the mosaic structure, which has been left aside in the diagram, but will influence the result of the process. The picture nevertheless makes it plausible to suppose that when large numbers of dislocation lines have been stopped at A' and B', the region between these points may be able to show a rotation over a considerable angle. It is probable that such a process* is the cause of the lattice curvatures observed by W. G. Burgers[11, 12, 13]. It is not impossible that, as W. G. Burgers observes, an important part of the region *abcd*, although it is subjected to large stresses, may keep a fairly regular structure, while the irregularities are heaped up near A' and B'. As has been remarked above,

* The observations of Andrade and Roscoe[14] on the ends of the slip bands are of interest in this connexion. These authors assume that in such cases the two groups of dislocations have just passed each other; as far as I can see, however, such a situation will not lead to a satisfactory picture of the local deformation. It is possible also, that when a group of dislocation lines coming from one side has been stopped and has called forth a large local deformation at some spot, a number of the original dislocation lines, belonging to the transition surface between two domains of the mosaic, may be driven out through the lattice.

however, it is difficult to work out a detailed model picture of the type and distribution of the structural irregularities to be expected here.

§ 10. SHEAR HARDENING AND RECOVERY

With reference to the situation pictured in figure 9, it is further to be observed that as far as the fields of stress connected with the segments of dislocation lines at A' and B' perpendicular to the plane of the diagram are concerned, these fields on the average will have positive shear stresses in the region between A' and B' and negative shear stresses in the regions to the left of A' and to the right of B', positive and negative (with reference to the shear to which the crystal is subjected) being taken as indicated in the diagram. Hence at the surfaces of the crystal where the new dislocation lines originate, the interior or induced stresses due to the stopped dislocations counteract the exterior stress to a certain extent. It is to be expected that in this way a kind of protection for the crystal will be obtained; the formation of new dislocation lines will become less frequent, and thus we arrive at the possibility of an explanation of the shear hardening, which has been set forth elsewhere[12, 15].

It may be assumed, finally, that crystal restoration is a phenomenon producing a gradual removal of the local deformation, caused by the stopping of dislocations. Here again, however, a more detailed investigation, in particular of the geometrical aspects of the process, will be necessary before the elementary phenomena which play a part can be understood in a satisfactory way. It may be supposed, for instance, that one elementary phenomenon of the restoration process is formed by shifts of the transition surfaces between the domains of the mosaic, by which a release of interior stresses may be brought about. Perhaps another phenomenon might be the migration of pairs of dislocations towards the exterior surface of the crystal.

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THE SIZE OF A DISLOCATION

By R. PEIERLS, The University, Birmingham

ABSTRACT. Calculations are made of the size of a dislocation and of the critical shear stress for its motion.

It is generally supposed that the plastic deformation of crystals proceeds by means of the propagation of dislocations along the slip planes. Since a dislocation consists of a displacement of a great many atoms, it is obviously impossible to obtain a rigorous solution of the equilibrium conditions for all these atoms. Dr Orowan has shown me how to obtain an idealized model, which leads to equations that can be solved, of the forces in a dislocation, and in this note I shall report on the results.

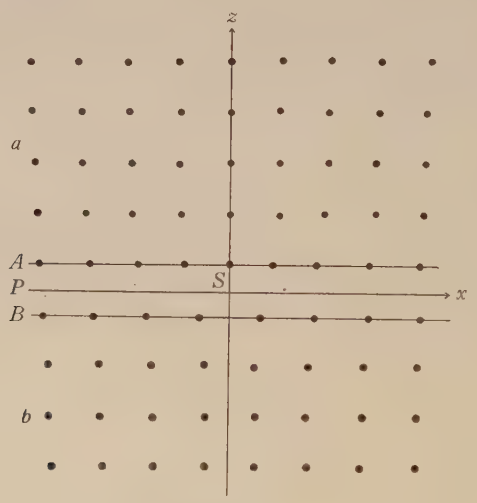

Figure 1.

The type of dislocation which I have investigated is sketched in figure 1. The slip plane P ($z=0$) divides the crystal into an upper part a and a lower part b. These are symmetrical about the vertical plane S ($x=0$). The central plane S lies in a net plane in the upper half-crystal a, and half way between two net planes in b.

The y axis at right angles to the plane of the figure (i.e. the line in which the plane S meets the slip plane P) is called the *dislocation line*. In the neighbourhood of this line the atoms of a are moved inwards and those of b are moved apart, so that at great distances from the dislocation line the two planes A and B which are immediately above and below the slip plane are again in correct alignment, A containing, however, one row of atoms more than B.

The atoms in the plane A are then subject to two forces: (i) The interaction

with other atoms in the half-crystal *a*. This force tends to spread the compression uniformly over the plane *A*, i.e. to extend the dislocation. (ii) The interaction with atoms in *b*, in particular with those in the adjacent layer *B*. This has a tendency to bring as many atoms of *A* as possible into correct alignment with *B*, i.e. to shorten the dislocation.

In equilibrium these two forces balance.

If the extension of the dislocation is large compared with the atomic distance *d*, both the horizontal displacement u and the vertical displacement w of the atoms in *A* vary slowly from atom to atom. The relative displacement of neighbouring atoms within each half-crystal is then much smaller than *d*. In these circumstances we may consider each half-crystal as an elastic continuum. Moreover we assume it to be an isotropic continuum, for the sake of simplicity. Then the force (i) is simply the force that has to be applied to the plane surface of an elastic continuum in order to make its horizontal displacement at the surface equal to $u(x)$. This force can be obtained by the usual methods of the theory of elasticity.

To the same degree of approximation, we may assume that the horizontal component of the force (ii) depends only on the horizontal displacement of the atoms of *A* relatively to the atoms of *B* immediately underneath. If $u(x)$ and $\bar{u}(x)$ are the two displacements, the force acting on a surface element near x is a periodic function of $u-\bar{u}$ with the period *d*. We may expect it to be very nearly a simple periodic function, i.e. to have the form

$$\text{constant} \times \sin\{2\pi(u-\bar{u})/d\}. \qquad \text{.....(1)}$$

The constant can be found from the shear modulus, provided it is assumed that the force arising between two lattice planes in a state of shear is independent of the displacement of the other lattice planes. This assumption is not strictly correct, but it is probably a reasonable approximation.

Further, it is assumed that the vertical component of the force (ii) depends only on the relative vertical displacement in *A* with respect to that of *B*. Since it follows from symmetry that the vertical displacements of *A* and *B* are equal, the vertical force (ii) is then equal to zero. This assumption again is not actually correct, since in places where the atoms in the two planes are out of alignment the equilibrium value of their vertical distance will obviously be changed. A separate discussion is required in order to take this effect into account, but for this one would have to specify the type of crystal one is dealing with and the direction of the slip plane.

With these approximations, the condition for the balance between the forces (i) and (ii) can be expressed by the following equation:

$$\int_{-\infty}^{\infty} \frac{\left(\frac{d\phi}{dx}\right)_{x'}}{x-x'}\,dx' = \frac{1}{2(1-\sigma)}\sin\frac{2\pi\phi}{d}, \qquad \text{.....(2)}$$

in which σ is Poisson's ratio, and $\phi = u-\bar{u}$. The solution is

$$\frac{\phi}{d} = \frac{1}{\pi}\tan^{-1}\left\{\frac{x}{d}(1-\sigma)\right\}, \qquad \text{.....(3)}$$

which shows that the extension of the dislocation is small and that the displacement has reached half its maximum value at a distance of $d/(1-\sigma)$ from the central plane S. This result indicates that we were not actually justified in our fundamental assumptions, which took the extension of the dislocation to be large. But the dislocation cannot, in any case, be much larger than we have found, since the equations ought to be correct if it were.

The next question is that of the motion of a dislocation under an external stress. As long as we retain the approximation of an elastic continuum for the crystal, it is evident that any stress, however small, will set the dislocation into motion. The reason is that, in our approximation, the energy of a dislocation is independent of its position; thus the dislocation is always in neutral equilibrium, and will move under any force. An external stress produces indeed a force that tends to move the dislocation since, if the dislocation moves by δx, the distant parts of a and b move relatively by $\delta x/N$, N being the number of atoms contained in the width of the crystal.

On the other hand, if the atomic structure is taken into account, the energy of a dislocation must, in the absence of a stress, depend on its exact position, i.e. on whether the plane of symmetry passes through a row of atoms or not. Hence the dislocation will have a number of stable-equilibrium positions, and these will persist even under a stress until this exceeds a certain magnitude.

A very rough idea of the variation of the energy with the position of the dislocation, and hence the critical stress, may be obtained in the following way. As long as the forces within each half-crystal are elastic, it is possible to express the total energy as a sum of terms involving only the displacements of the atoms in the two surface layers A and B. These displacements are, at each point, very little different from the displacements at the same point of the elastic continuum, as given by equation (3). Whereas, however, the energy of the continuum is to be obtained by integrating over the slip plane, we must now sum it over all atoms in the slip plane. The sum depends on the exact position of the centre of the dislocation, whereas the integral does not. We are therefore concerned with the difference between the sum and the integral. Now it is known that in sums of this type, in which the summation extends from $-\infty$ to $+\infty$, and in which the summand is a smooth function of the variable, the difference between sum and integral is extremely small; moreover, it decreases rapidly with increasing size of the dislocation.

If one tries to estimate on this basis the critical shear stress σ_c in terms of the shear stress σ_t that would be required to make an undistorted lattice plane slip uniformly over the adjacent plane, one finds that this ratio is given approximately by

$$\frac{\sigma_c}{\sigma_t} \simeq \frac{4\pi}{1-\sigma}\{5{\cdot}8 - \log(1-\sigma)\}\, e^{-4\pi/(1-\sigma)}.$$

When $\sigma = 0{\cdot}4$, this is about 10^{-7}.

No reliance can be placed on the actual order of magnitude of this result, since it is extremely sensitive to the simplifying assumptions which have been made,

and an improved discussion may considerably alter the order of magnitude. In spite of this, it seems safe to draw the following conclusions: (i) The extension of a dislocation, i.e. the width which contains all atoms whose displacements with respect to their neighbours exceed, say, $d/4$, is not appreciably larger than the atomic distance, and depends on Poisson's ratio. (ii) Under the influence of an external shear stress the dislocation will move, provided that the shear stress exceeds a critical value. This value is smaller by several powers of ten than the so-called theoretical shear stress, i.e. the stress required for uniform slip. (iii) In our present approximation the critical shear stress depends strongly on Poisson's ratio. If the anisotropy of the crystal is taken into account, it will instead depend on some other combination of the elastic constants, different for each plane. It will, however, also be influenced by the anharmonic forces between the atoms, which have here been neglected, since the displacements near the dislocation line are large.

SOME THEORETICAL PROBLEMS CONCERNING THE SOLID STATE

By J. E. LENNARD-JONES

ABSTRACT. This paper contains a discussion of some of the unsolved theoretical problems connected with the solid state of matter. One of these is the occurrence of small crystallites even in the most perfect crystals. Reasons are given for attributing such imperfections in crystals to the conditions of growth from the melt. It is pointed out that a study of the conditions prevailing at the boundaries between crystallites might throw light on slip and on the appearance of slip bands—properties of crystals which have not yet been adequately explained. The nature of melting and the converse process of solidification require further study. Local melting may occur in crystals owing to slip and be a factor in producing strain hardening. A method is given of evaluating the relation between stress and strain outside the usual elastic limits and at temperatures approaching the melting temperature.

§ 1. IMPERFECTIONS IN CRYSTALS

Some of the theoretical problems concerning the properties of solids under stress have been admirably summarized in recent articles by W. G. Burgers[1] and J. M. Burgers[2]. It appears that while theory can deal with perfect solids, once the interatomic forces are known, there is no adequate or satisfactory theory of actual solids. Thus calculations of the elastic constants of such solids as ionic crystals[3], like rocksalt, or metallic crystals, like copper[4], have been made and are in substantial agreement with experiment, provided that the observations are carried out under conditions approaching those assumed in the theoretical calculations; that is, the strains set up must be small and the solid must return to its original form when the stress is removed. By extensions of these calculations it is possible to derive a theoretical estimate of the stress necessary to produce breakdown, either in elongation or in shear, assuming the solid to remain everywhere homogeneous. These estimates are, however, far in excess of the stresses which solids can stand without drastic deformation. Many solids begin to suffer from plastic flow for quite small stresses. This fact and experimental evidence of a direct kind have necessitated the conclusion that solids are rarely, if ever, perfect crystals, and that the slip, which occurs along crystallographic planes, is not simply a gliding of one perfect crystal lattice plane over another. The problem then arises as to why actual crystals, even those grown under very carefully controlled conditions, are so imperfect.

It has been suggested that a solid might be more stable in a form in which there are regions of perfect crystal structure, separated at fairly regular intervals by flaws

or regions of disorder, the latter forming a secondary structure. Detailed considerations of the free energy of a solid under such conditions negative that hypothesis. There can be no reasonable doubt that the state of lowest free energy would be that of a perfect crystal if the conditions necessary for attaining it could be achieved. Moreover, it is difficult to believe that such a solid would not have the elastic properties indicated by theory. It is sometimes asserted[5] that a perfect crystal might be so weak as to be incapable of supporting its own weight, but there is no direct evidence for this suggestion, and, in the absence of any observation to support it, it seems reasonable to accept the indications of theory that perfect crystals, however small, would be stable and strong at temperatures well below the melting point.

The picture of a crystal accepted at present is that it consists of small domains or crystallites in which the atoms form a perfect lattice system. Estimates of the size of these regions differ but they do not vary widely from an average length of 10^{-4} cm. They may be greater or less than this, according to the conditions of growth, but it is surprising and significant that this figure should occur so frequently in the literature, obtained by such a variety of experimental methods. A satisfactory explanation of this feature has yet to be given.

In a single crystal these small domains appear to be inclined at small angles to each other, at any rate that is the indication of x-ray analysis. This has been discussed by Ewald and Renninger[6], who have shown how the observations can be interpreted so as to give information about the size of coherent domains and their orientation relative to one another. Incidentally, it should be mentioned that they found in certain specimens of artificially grown crystals regions of perfect structure exceeding a size of 10^{-4} cm., probably of the order of 10^{-3} cm. or more.

In seems clear that the degree of imperfection of a crystal, both as regards the size of the perfect domains and the disarrangement in orientation, depends on the conditions under which the crystal is grown. This suggests that it would be profitable to make a detailed study of the mechanism of solidification. The author and A. F. Devonshire[7] have recently given a theory of the process of fusion, but it is assumed in the theory that thermodynamic equilibrium is attained at each stage of the process, and that the temperature is everywhere uniform. This implies a very slow change of state. In practice it is certain that there will be temperature-gradients during the process of solidification, for the latent heat of fusion given up by small domains on freezing will only be conducted away at a finite rate.

The speed at which solid domains grow will be determined by two factors. The first will be the rate of diffusion of atoms from the adjoining liquid. This will govern the rate at which the atoms can get into the right places near the surface of the solid, that is, the rate at which a state of disorder can be changed to one of order. The second factor will be the rate of diffusion of atoms along the surface of the solid to a suitable vacant place in the lattice, as shown in Volmer's experiments on crystal growth[8]; a theory of this has been given by the author[9]. The energies required for these two processes may be of the same order, or one of them may predominate and be the rate-determining factor.

Eventually the solid domains will meet, just as colloidal particles do in a concentrated solution, that is to say, at a number of finite points. At first there will be no correlation between the orientation of a domain and those of its neighbours. The domains will try to turn so as to get into proper alignment with each other, so that the crystal axes are parallel, but it will clearly be difficult for any one domain to satisfy all its neighbours at once. It is at this stage that it will be difficult to preserve thermodynamic equilibrium. The process must be a co-operative one, just like the rotation of irregularly shaped molecules in the solid state. Moreover, it can only take place while the intervening matter is still liquid. The time factor is thus of the greatest importance. The system must be given a long time to overcome the energy barriers necessary for rotation owing to the irregular shapes, and to settle down to a set of coherently arranged domains. We may imagine the system as very similar to a set of icebergs in an ice pack, each blocking the rotation of another.

This picture allows us to understand some of the observed properties connected with the production of single crystals. Thus the method of Carpenter and Elam[10] is to stretch an imperfect crystal slightly and then gradually heat it to a temperature just above the melting point. The method clearly produces conditions in which domains can change their orientation relative to one another or grow at the expense of one another.

If the conditions necessary to produce coherent growth are considered in detail, the surprising thing is not that single crystals are rarely produced in Nature, but that crystals should ever be produced at all with anything like perfection.

There is one further remark which may be made concerning the process of crystal growth. When the crystal nuclei are large enough to touch each other, the remaining liquid will be held in the interstices and, being near the freezing point, will be in a highly viscous state. Diffusion of the liquid through the gaps connecting one region of liquid with another will be comparatively slow. If the liquid in any one intersticial region freezes before the adjoining crystal nuclei have become properly aligned, there will be competing claims imposed on the region as to the state of order to be followed. The result will be a measure of disorder within this region. Moreover, freezing usually causes a diminution of volume. Up to the last stages of solidification this can be accommodated by the flow of liquid from one part to another, but there will come a time when this is no longer possible. The final contraction of the last remaining portions of liquid will then occur in separated regions and will produce holes of atomic size within them. This suggests the occurrence of flaws of atomic size between perfect domains.

§ 2. SLIP IN CRYSTALS

Another problem of great importance is the mechanism whereby slip occurs when single crystals are subject to stress. One of the most attractive of the theories which have been proposed in explanation of this process is that of G. I. Taylor[11]. According to this theory, slip is caused by the propagation through a crystal of dislocations, which consist of local irregularities in the arrangement of atoms.

Under the influence of stress these move in such a way as to cause a net movement of an amount of one atomic spacing of one part of a crystal relative to the rest. Reasons are given for supposing that the transmission of a dislocation, once formed, through an otherwise perfect domain of crystal can be effected by a very small shearing stress. These dislocations are supposed to be created at the boundary, or within a crystal, as a result of thermal motion. The observed slip of crystals along certain crystallographic planes is attributed to the additive effect of a large number of dislocations.

The resistance to motion of these dislocations is due to their interaction with each other. They are of two types, positive and negative, and those of like sign cause stresses in the immediate neighbourhood which produce a repulsion between dislocations of the same sign and an attraction between those of opposite sign. They therefore tend to arrange themselves like a lattice, each positive dislocation being surrounded by negative ones and vice versa. For simplicity the dislocations are assumed to be two-dimensional, in the sense that they have the same form for all sections parallel to a given plane. They have an axis like linear vortices, to which in some respects they are closely analogous, and move forward in a direction perpendicular to the axis.

According to this, model dislocations move forward until they meet a flaw or other termination of a regular crystal domain. If the average distance be L and the interatomic spacing be λ, the mean shear produced by the dislocations, when there are n of them per unit area perpendicular to their axes, is found to be given by[17]

$$\gamma = L\lambda n. \qquad \ldots\ldots(1)$$

The stress necessary to move one set of dislocations relative to the other of opposite sign against their mutual interactions is found to be

$$f = CG\lambda n^{\frac{1}{2}}, \qquad \ldots\ldots(2)$$

where C is a constant and G the modulus of shear. By elimination of n, it is thus found that γ is proportional to f^2, and this is in accord with the observation that there appears to be a parabolic relation between strain and the critical shear necessary to produce it. By a comparison of the theoretical relation and that observed, a value for L is found which varies from substance to substance but is of the order of 10^{-4} cm. in all substances.

This theory has many attractive features, but on closer examination it is found to involve certain difficulties. Its chief success is obtained by eliminating n, the concentration of dislocations, but if, a value having been obtained for L, use be now made of the formula for γ to find a value of n, it appears that for a shear strain of the order of 10^{-1}, $n\,(=\gamma L^{-1}\lambda^{-1})$ must be of the order of 10^{11} per cm.^{2} This implies that each small crystallite contains at any moment about 1000 such dislocations parallel to each of its principal axes. This is a very large number. It is nearly equal to the number of atoms along any one edge of the domain, and so we must conclude that each row of atoms on the surface of a crystallite is responsible for one of the dislocations in transit at any moment.

It seems desirable therefore to consider other possible mechanisms of slip, or modifications of the dislocation hypothesis. It may be profitable to examine in some detail the conditions obtaining at the surface of the small crystallites. A nearly perfect crystal may contain surfaces of misfit such as those shown in figure 1, in which two domains, each of perfect crystal structure, meet at an angle (exaggerated in the figure). Actually, atoms at the boundary will have to accommodate themselves as best they can to the conflicting claims of both domains, and the result will be that they will all be pulled out from their normal positions in the crystal plane and take up irregular positions so as to make the free energy a minimum. We assume for the present that this change will be small.

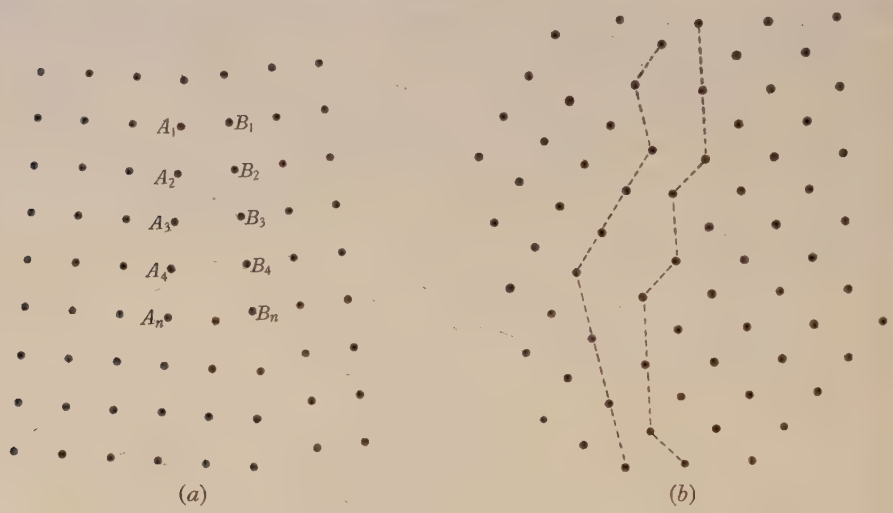

Figure 1. A diagrammatic representation in two dimensions of surfaces of misfit: (*a*) shows the meeting of (1, 0) planes and (*b*) the meeting of (1, 1) planes. The left-hand and right-hand portions, as shown, are each perfectly arranged and are so adjusted that there is no gap between them as great as twice the normal spacing.

The difference between the free energy which the assembly would have if the atoms formed a single perfect lattice, and that which they have in the arrangement shown, could be regarded as a surface tension, associated with the common boundary of the two regions. Owing to the fact that some of the atoms are held in common by the two lattices while at other places there is no such coincidence, the surface tension will change markedly from point to point on the boundary layer. In some portions these stresses will tend to expand the lattice, at others to contract it. Under these conditions there will be a tendency to produce within the layer dislocations of the Taylor type already discussed.

Another consequence of an ill-fitting boundary of this type will be that the cohesion between the two domains will depend mainly on a number of what are called "points of contact". Examples of such contacts are shown in figure 1, where one atom is seen to belong simultaneously to the two lattices. At other parts of the boundary layers the atoms of one lattice are well separated from those of the other lattice. The cohesion in these parts is considerably weakened.

A rough estimate of the change in potential energy due to a step-like joint may be made as follows. In figure 1 (*a*) two domains of perfect lattice structure are inclined at an angle θ, the next step occurring at B_n, where B_nA_n is of the order of twice the normal distance between nearest neighbours. Another atom can then be inserted between B_n and A_n. If the interaction of nearest neighbours is W and all other interactions are neglected, the change of potential energy of the pair A_2 and B_2 is $a\theta\,(dW/dr)$. Similarly, that of A_3 and B_3 is $2a\theta\,(dW/dr)$, and so on. The change $\Delta\Phi$ of potential energy of the whole step, assuming that dW/dr may be regarded as constant over the range a to $2a$, is then given by

$$\Delta\Phi = -\Sigma na\theta\, dW/dr = -\tfrac{1}{2}N\,(N+1)\,a\theta\, dW/dr, \qquad \text{.....(3)}$$

where N is the number of atoms in one step. Now the step comes to an end when $Na\theta = a$, so that

$$\Delta\Phi = -\tfrac{1}{2}\,(N+1)\,a\,dW/dr. \qquad \text{.....(4)}$$

This change of energy may be regarded as the main contribution to a surface tension, the change of other parts of the free energy being small in comparison. Denoting the surface tension by σ, and noting that the amount of new surface created by a slab of thickness a is $2Na^2$, we have

$$2Na^2\sigma = \Delta\Phi, \qquad \text{.....(5)}$$

so that

$$\sigma = -\tfrac{1}{4}a\,(1+1/N)\,dW/dr. \qquad \text{.....(6)}$$

This is seen to be insensitive to the length of the step, provided N is fairly large. Actually, this expression gives only the average surface energy, for, as is evident, the change of energy of each atom in the row B_1 to B_n is different. If the forces on each were considered in detail, it would be seen that there is a non-uniform stress set up in the two surfaces A_1A_n and B_1B_n.

If the energy required to break a perfect crystal across a plane such as A_1A_n is equal to Φ_0 per unit area, the energy required to break the crystal across the step-like structure shown in figure 2 will be given by

$$\Phi_0 - \frac{\Delta\Phi}{Na^2} = \frac{W}{a^2} + \frac{1}{2a}\left(1+\frac{1}{N}\right)\frac{dW}{dr} \simeq \frac{1}{a^2}\left(W + \frac{a}{2}\frac{dW}{dr}\right), \qquad \text{.....(7)}$$

which is approximately the energy per unit area required to separate two planes from a distance $3a/2$ apart. This will in general be considerably less than Φ_0.

The next problem to consider is the method by which shear could occur along such a step-like boundary. We assume that the domains make perfect contact only at one in every N atoms and that the surfaces consist of a set of regular steps. For simplicity we take the structure to be the same in every plane parallel to that shown in figure 2, so that every atom shown corresponds to a regular row of atoms perpendicular to the plane of the paper. It also simplifies the problem if the steps be all assumed to be on the right-hand surface, that of A_1A_n being perfectly plane.

For this model we observe that if the right-hand domain is moved an atomic distance parallel to A_1A_n, all the conditions are reproduced. The field on the domain as a whole is periodic in this direction. To move the whole domain rigidly

it is, however, necessary to tear apart all the points of contact simultaneously. But an easier method can be effected by using the elastic properties of the parts of the crystal which form the connecting links between the points of contact. Thus we may suppose one point of contact to be dragged forward relative to A_1A_n owing to a force applied from below. The next point of contact will not move until the elastic stress in the material connecting it to the first has reached a certain lower limit. This may not occur until the first has moved forward and become anchored again.

The problem is similar to that presented by the motion of a number of particles of mass m, arranged in a line and each connected by springs to its two neighbours, when the surface on which they rest has a wave-like form, figure 2. When a force F is applied to the end one, it may move forward one or more waves of the surface before the tension in the connecting spring is sufficient to drag the second one over the potential barrier separating it from the next trough.

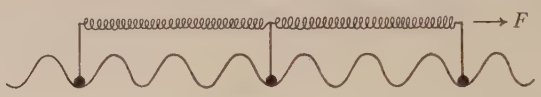

Figure 2

The equations of motion for such a system may be written in the form

$$\left.\begin{aligned} m\ddot{x}_1 &= F-k\,(x_1-x_2)-P\sin\,(2\pi x_1/a)\\ m\ddot{x}_2 &= k\,(x_1-x_2)-k\,(x_2-x_3)-P\sin\,(2\pi x_2/a)\\ \ldots\quad &\ldots\quad\ldots\quad\ldots\quad\ldots\quad\ldots \end{aligned}\right\} \qquad \ldots\ldots(8)$$

If there were n particles and if, instead of being connected by springs, they were connected rigidly, it would be necessary for F to exceed nP before a sufficient movement could take place to take each particle into the next trough. This need not necessarily be so when they are connected elastically, for we have

$$m\,(\ddot{x}_1+\ddot{x}_2+\ldots)=F-\Sigma P\sin\,(2\pi x_n/a), \qquad \ldots\ldots(9)$$

and if phases x_1, x_2, ... of the particles adjust themselves suitably, the summation on the right-hand side may be considerably less than nP. Thus, if there were only two particles and the connecting spring remained stretched so that

$$x_1-x_2=(2r+1)\,a/2,$$

where r is any integer, then the effect of the corrugations in the field would disappear. It would appear that a force F, such that $P<F<2P$, would then be sufficient to produce a forward motion of the two particles. It would be instructive if a mathematical solution of these equations could be found*. It appears probable that the motion of the first particle will be of an oscillatory character but with a net movement forward. In the case of only two particles a possible mechanism would be for the *average* extension of the spring to be $a/2$, with oscillations about it, the whole system meantime moving forward as a whole.

This model suggests a mechanism whereby slip may occur in a crystal by a movement of one crystallite over another. It is evident from what has been said

* (*Added in proof.*) This problem has now been considered and a discussion will be published shortly by Devonshire, Corner and Wilkes.

that the stress necessary to produce slip of this kind may be only a fraction of that necessary to make one perfect lattice layer move over another parallel one. Moreover, it treats the phenomenon as a dynamic process and introduces a frequency $(k/m)^{\frac{1}{2}}$ and so a unit of time $(m/k)^{\frac{1}{2}}$ which will determine the rate at which a disturbance is propagated along the chain. Since k in the actual problem can be expressed in terms of the elastic properties of the perfect crystal bridging adjacent steps (thus $k \simeq c_{11}/Na$, where c_{11} is defined in the usual way as the ratio of stress to strain in the direction of one of the crystallographic axes, and Na is the distance between one step and the next), the velocity with which the forward velocity of the steps is transmitted along the boundary of a domain can be expressed in terms of the velocity of the elastic waves of the crystal.

It is clear that a Taylor dislocation could be considered in a similar dynamic way. In this case, however, the distance between nearest neighbours in the dislocation never differs much from an interatomic spacing, and so the appropriate analogy along the lines of figure 2 would be for the particles to be in every hollow. This implies that the appropriate k is given by c_{11}/a, and so the analogous connecting springs are much more rigid than in the process just considered. This is obvious when it is recognized that in both cases it is necessary to stretch the connecting spring a length a to produce a unit jump forward, and this requires a strain of $1/N$ in the one and a strain of unity in the other.

So far we have neglected the effect of temperature. This will modify the problem considerably, for, referring to the model as represented in figure 2, we must now suppose the wave-like surface to possess energy and to be capable of absorbing and emitting energy to the system of weights and springs. The same state of affairs exists when gas atoms are adsorbed on a solid surface. In this case, as is well known, surface migration occurs and may be attributed to the communication of energy from the solid below.

We consider first the motion of a single particle under these conditions. The height of the potential barrier separating one trough from the next is Pa/π, and the probability that the first particle will have this energy will be proportional to $\exp(-Pa/\pi kT)$. If c is the average velocity appropriate to an energy of this amount, the probability of a jump in either direction per unit time will be of the order

$$(c/a)\exp(-Pa/\pi kT). \qquad \text{.....(10)}$$

When, however, there is an applied force F from left to right, the energy necessary to go from left to right over a barrier is only $Pa/\pi - Fa/2$, while that necessary to go from right to left is $Pa/\pi + Fa/2$. Hence the net probability of a jump towards the right per unit time will be of order

$$\begin{aligned}(c/a)\exp(-Pa/\pi kT)\,[\exp(+Fa/2kT)-\exp(-Fa/2kT)]\\ = 2\,(c/a)\exp(-Pa/\pi kT)\sinh(Fa/2kT). \qquad \text{.....(11)}\end{aligned}$$

If we suppose that the particle gives up its excess energy to the underlying solid when it gets to the next trough, its average velocity forward is

$$2c\exp(-Pa/\pi kT)\sinh(Fa/2kT). \qquad \text{.....(12)}$$

In the particular case when $Fa/2$ is small compared with kT, this expression simplifies to

$$Fac/kT \exp(-Pa\pi/kT),$$

and then we get a net creep forward at a rate proportional to the applied force.

From this analogy we may construct the following picture of what happens at the boundary of two crystallites. Each point of contact will move backwards and forwards at a rate given by an expression like (10), modified to take into account the elastic energy necessary to move one point of contact relative to other neighbouring points of contact. If the connecting bridges are sufficiently long, this extra energy will be small compared with that required to surmount the energy barrier at contact. Moreover, it will affect to the same extent the probability of a jump in any direction, at any rate at first.

If there are n points of contact per unit area, supposed to be equally spaced, and S is the applied shearing stress per unit area, while L is the thickness of each crystallite, then the stress acting at each point is SL/n. Denoting by E the energy required to move a point of contact an atomic spacing, we find, by a method similar to that used in deriving equation (12), that the average forward velocity of each point of contact in the direction of the applied stress is

$$2c \exp(-E/kT) \sinh(SLa/2nkT), \qquad \text{.....(13)}$$

and so this is the average velocity of one crystallite over another. As has already been explained, the argument is only valid provided that the spacing between one point of contact and the next is large compared with an atomic spacing; otherwise the movement of the points of contact cannot be reckoned as independent. The rate of shear strain is then

$$\frac{d\gamma}{dt} = \frac{2c}{L} \exp\left(-\frac{E}{kT}\right) \sinh \frac{SLa}{2nkT}, \qquad \text{.....(14)}$$

and the coefficient of plastic flow ζ, defined by

$$\zeta \frac{d\gamma}{dt} = S,$$

is given by

$$\zeta = \frac{SL}{2c} \exp \frac{E}{kT} \div \sinh \frac{SLa}{2nkT}. \qquad \text{.....(15)}$$

This quantity is analogous to the coefficient of viscosity of liquids. For small shearing stresses we find

$$\zeta = \frac{nkT}{ac} \exp \frac{E}{kT}, \qquad \text{.....(15}a\text{)}$$

a relation which is similar to that usually given for the viscosity of liquids. In the latter case the relation is confirmed by experiment as regards dependence on temperature.

As has been indicated above, however, it will be necessary in developing a theory on these lines to take into account the elastic energy of the crystal when one point of contact moves in relation to its neighbours. This will introduce into

equation (10) and subsequent expressions a term similar to that found by Becker[12] and Orowan[13] in considering temperature fluctuations of the elastic energy stored up in each element of volume.

§ 3. THE PROBLEM OF MELTING

In order to arrive at an understanding of the nature and detailed structure of actual solids it may be necessary, as has been pointed out above, to study the process of melting and solidification. Not only the occurrence of flaws and the disorientation of crystallites but also such properties as shear hardening may find a ready explanation when the effects of time and external stresses on the mechanism of solidification are known.

In this connexion attention may be called to the experiments of Bowden and Leben[14] on the nature of sliding friction and the contact between solid surfaces. They find that sliding between clean surfaces takes place in a series of jerks, and produce evidence to support the view that the area of intimate contact may be only 1/10,000 of the apparent area, and that sliding consists in the alternate formation and rupture of metallic junctions. Something of the nature of local melting may occur as a result of the stresses imposed, followed by immediate solidification as soon as heat is conducted away.

A somewhat similar process on a microscopic scale may occur in the process of slip in single crystals. The heat developed by the relative displacement of atoms, as considered in the preceding section, may cause rapid heating and cooling along the boundaries of crystallites, which will upset the regularity of the crystal lattice. A comparison of Laue spots before and after straining suggests that some of the planes in crystallites have been rotated, and the conditions along crystallite boundaries may be severely changed. It is not the object of this paper to consider this process in detail, but rather to suggest the effect of temperature fluctuations during slip and to point out the need for a theory of melting.

In recent papers, A. F. Devonshire and the author[7] have suggested an elementary mechanism or model by which a change from a solid to a liquid state may take place. According to this theory atoms are allowed, if they have sufficient energy, to take up positions off the normal lattice sites. In the theory of order and disorder in alloys[16] it is supposed that there are a definite number of lattice sites and that each is occupied, though the type of atom at a lattice point may depend on the type of order or disorder present. In other words, the probability of occupation of a lattice site is always unity. Supposing now that we deal in terms of probabilities, as in the modern theory of electrons in atoms and molecules, we can to a first approximation associate a probability Q with each lattice site. Higher approximations may be necessary to take into account the effect of the occupation of one site on other neighbouring sites, but we may neglect that correlation to begin with.

A value 1 of Q corresponds to a perfect solid, such as we may imagine to exist at the absolute zero. When, at higher temperatures, Q becomes less than unity, we must ask where the remaining atoms go to. To be definite we consider a face-

centred cubic lattice and label the normal lattice points as α sites. If each such site be weighted to an extent Q as a centre of force, and the field of force due to the array be plotted, it will be found that there are certain positions between the α sites for which the potential energy has a stationary value. These sites interpenetrate the normal lattice sites in the same way that the chlorine ions of rocksalt interpenetrate the sodium ions. We call them β sites. The energy associated with them depends on Q but is usually higher than that of a normal site, though it is less than its own immediate neighbourhood. If N is the total number of atoms, then NQ is the number on the α sites and the rest, $N(1-Q)$, may be expected to be primarily on the β sites, since these are the positions of next lowest energy.

Let the energy of interaction of two atoms in adjacent α and β sites be W. Then the average energy of an atom in a β site, when the probability of occupation of an α site is Q, is

$$W_\beta = 6WQ, \qquad (16)$$

since there are six surrounding α sites. Similarly, the average energy of an atom in an α site is

$$W_\alpha = 6W(1-Q). \qquad \ldots\ldots(17)$$

Since there are NQ atoms on α sites and $N(1-Q)$ on β sites, the total energy of interaction of α and β pairs is

$$NQW_\alpha = N(1-Q)\,W_\beta = 6NWQ(1-Q). \qquad \ldots\ldots(18)$$

If the energy of interaction of two atoms on neighbouring α sites be ϕ, then the mutual energy of all the atoms on α sites is

$$\tfrac{1}{2}\{12N\phi Q^2\} = 6N\phi Q^2, \qquad \ldots\ldots(19)$$

since there are 12 neighbours. Similarly, the energy of the β set is

$$6N\phi(1-Q)^2, \qquad \ldots\ldots(20)$$

and so the extra potential energy U'' of the system as a result of disorder* is given by

$$\begin{aligned} U'' &= 6N\{\phi Q^2 + \phi(1-Q)^2 + WQ(1-Q)\} - 6N\phi \\ &= 6NwQ(1-Q), \qquad \ldots\ldots(21) \end{aligned}$$

where

$$w = (W - 2\phi). \qquad \ldots\ldots(22)$$

Now the number of ways of distributing N atoms, so that NQ are on one set of N sites and $N(1-Q)$ on another set of N sites, is

$$\gamma(Q) = \{N!/[NQ]!\,[N(1-Q)]!\}^2. \qquad \ldots\ldots(23)$$

From (21) and (23) it can be deduced that the contribution to the free energy of the system is given by

$$A'' = 6NwQ(1-Q) + 2N\boldsymbol{k}T\{Q\log Q + (1-Q)\log(1-Q)\}, \qquad \ldots\ldots(24)$$

* I am indebted to Dr J. K. Roberts for pointing out to me that the value of U'' is given by equation (21) and not by equation (18), as was suggested in *Proc. Roy. Soc.* A, **170**, 469, equation (6), (1939). The interpretation given to W in that paper should therefore apply to w. Otherwise the theory is not altered.

provided that the value of Q used in this expression is such as to make

$$\gamma\, Q \exp\left(-U''/kT\right)$$

a maximum. This condition is given by

$$(2Q-1) = \tanh 6w\,(2Q-1)/4kT. \qquad \ldots\ldots(25)$$

We thus see that the disorder contributes an extra term to the internal energy of the system and an extra term $-2Q \log Q - 2\,(1-Q) \log (1-Q)$ to the entropy. In consequence there is an extra contribution to the pressure due to disorder, which is a function of volume and temperature. For a given temperature this disorder pressure is found to be small for small volumes, to rise to a maximum, and then to diminish again to zero for large volumes. When this pressure is added to that due to the thermal vibration of the atoms in an ordered assembly, the resulting isotherm has a shape similar to that characteristic of a liquid-vapour change of phase, that is, the pressure falls at first as the volume increases, then rises to a

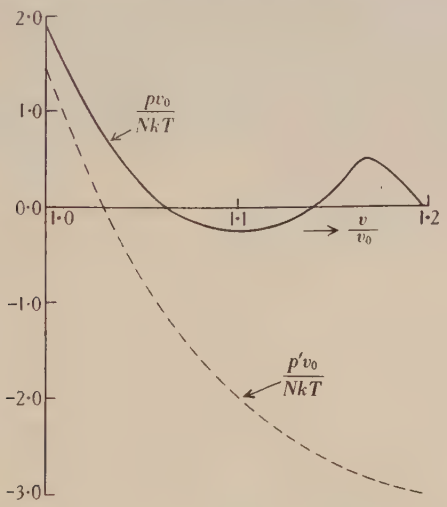

Figure 3. The relation between pressure and volume for a constant temperature, showing a change of phase from solid to liquid. The dotted curve gives the same relation when perfect order is assumed.

maximum, and finally falls again. As in the theory of evaporation, not all states on this isotherm are thermodynamically stable, and the sigmoid part has to be replaced by a straight line. A change of state along this line corresponds to the spreading of disorder throughout the assembly and is associated with the process of melting.

This model is undoubtedly an oversimplified version of the way in which melting occurs in Nature, but it does reproduce the main features of the phenomenon in that it shows how a change of volume occurs and gives some insight into the nature of latent heat. Numerical calculations of these quantities for substances such as argon and nitrogen, for which the interatomic forces are known, have resulted in values in substantial agreement with experiment. What is now required is an extension of this theory to take into account the time factor, so that calculations may be made of the *rate* at which melting or solidification occurs.

§ 4. A SOLID IN A STATE OF STRESS NEAR THE MELTING TEMPERATURE

The theory of the preceding section applies only to an assembly which is isotropic, so that the only independent variables defining the state of the system are volume and temperature, or alternatively pressure and temperature. However, pressure, as ordinarily understood, can only be positive and is usually taken to be isotropic. It seems desirable to extend the theory so that it may be applicable when a solid is in a state of inhomogeneous stress.

We suppose, as before, that the solid is a face-centred cubic lattice structure and that it is subject to stresses X_x, Y_y, and Z_z along the crystal axes. For a cubic crystal of this kind subject to *small* stresses there are only two independent elastic constants, and so it is only necessary to work out two cases, viz. (1) that in which $X_x = Y_y = Z_z$, for this gives the cubic compressibility and so $(c_{11} + 2c_{12})$, and (2) that in which $Y_y = -X_x$, $Z_z = 0$, for this gives $(c_{11} - c_{12})$. However, we shall not confine the theory to the usual small strains of the elastic theory.

Only a brief indication will be given here of a method of generalizing the work of the previous section. A model of the solid similar to that of Einstein may be used in which each atom is regarded as vibrating with the same frequency. If ν_0 be the frequency, the partition function of an ordered lattice of N atoms when subject to isotropic conditions is given by

$$[f(T)]^N \exp(-U_0'/\boldsymbol{k}T), \qquad \text{.....(26)}$$

where

$$f_0(T) = (2\lambda \boldsymbol{k}T/\boldsymbol{h}\nu_0)^3, \qquad \text{.....(27)}$$

and U_0' is the internal energy of the state in a state of order.

In the face-centred cubic lattice each atom is surrounded by 12 nearest neighbours. These are so arranged that when the central atom is at the centre of a cube, the nearest neighbours occupy the mid-points of the edges. We denote the length of each edge of this cube by c_0. It simplifies matters to concentrate on this unit cell when the crystal is subject to stress. For a system of stresses along the crystal axis this cube becomes a rectangular parallelopiped with unequal sides c_1, c_2 and c_3. This deformation has two important effects. Firstly it changes the potential energy of the central atom even when it remains at the centre of the cell. Secondly it changes the potential field about this equilibrium position, the equipotential surfaces being changed from spheres to ellipsoids. It is clear, however, that the principal axes of these ellipsoids will be the same as those of the crystal axes and that the normal modes of vibration will be along them, with frequencies which we may denote by ν_1, ν_2 and ν_3.

Under these conditions the partition function of the N atoms of the crystal will be

$$[f(T)]^N \exp(-U'/\boldsymbol{k}T), \qquad \text{.....(28)}$$

where

$$f(T) = (2\pi \boldsymbol{k}T/\boldsymbol{h}\nu_1)(2\pi \boldsymbol{k}T/\boldsymbol{h}\nu_2)(2\pi \boldsymbol{k}T/\boldsymbol{h}\nu_3), \qquad \text{.....(29)}$$

and

$$U' = \frac{N}{2}\phi(c_1, c_2, c_3), \qquad \text{.....(30)}$$

ϕ being the potential of each atom due to the rest. For known forces, ϕ and the frequencies ν_1, ν_2 and ν_3 can all be calculated as functions of c_1, c_2 and c_3. From the partition function (28) the free energy A' can then be deduced, and it also may be regarded as a known function of c_1, c_2 and c_3.

For temperatures approaching the melting temperature it may not be legitimate to use the approximation of normal modes, implied in equation (29). In this case it will be necessary to use a method similar to that adopted by the author and A. F. Devonshire in the theory of melting. There the concept of the average volume (v_f^*) available to each atom was used, and this volume was evaluated by weighting each element of volume accessible to the atom by a Boltzmann factor appropriate to the potential energy associated with it. In this way we should obtain instead of equation (29) an expression of the type

$$f(T)=(2\pi mkT/h^2)^{\frac{3}{2}}\, v_f^*, \qquad \text{.....(31)}$$

and for the free energy

$$A'=\tfrac{1}{2}N\phi\,(c_1, c_2, c_3)-NkT\log\{v_f^*\,(2\pi mkT/h^2)^{\frac{3}{2}}\}. \qquad \text{.....(32)}$$

This is probably a more reliable method of obtaining the free energy, for v_f^* is a quantity which must remain positive and clearly must increase steadily with temperature, whereas one or other of the frequencies used in equation (29) may appear to become imaginary under certain conditions.†

Now the change dA of free energy in a slight change of c_1, c_2, c_3 and T, due to a system of stresses X_x, Y_y and Z_z, each referred to unit area, is given by

$$dA=c_2c_3X_x\,dc_1+c_3c_1Y_y\,dc_2+c_1c_2Z_z\,dc_3-S\,dT, \qquad \text{.....(33)}$$

whence

$$X_x=\frac{1}{c_2c_3}\left(\frac{\partial A}{\partial c_1}\right)_{c_2, c_3, T}, \qquad \text{.....(34)}$$

and so on.

So far we have, in calculating the free energy, assumed the order of the crystal to be perfect, but, as in the theory of melting, it will be necessary at temperatures approaching the melting temperature to take into account the disorder which may exist in the arrangement of atoms. It is clear that a state of stress will produce conditions within the crystal favourable for disorder to occur, for the energy necessary to place an atom on an abnormal site will be diminished.

The state of disorder contributes a term similar to that given in equation (24) with w suitably modified to take account of the extension of the lattice. Hence, we have

$$A=A'+A'',$$

and substituting this expression in equation (34), we find that there are two contributions to X_x, viz.

$$X_x=X_x'+X_x'',$$

the first being the value appropriate to a perfectly ordered crystal and definite values of c_1, c_2, c_3 and T, while the second is the extra contribution due to disorder. The latter will have properties similar to the disorder pressure, discussed at the

† This is evident from figure 1 given by Lennard-Jones and Devonshire[15].

end of the preceding section, in that it will be small when the crystal is compressed and also when it is stretched by a large amount, for in the former condition the energy necessary to displace an atom to a position of disorder is large and consequently the disorder is small, while in the latter condition the disorder is large but the extra force exerted by an atom in a position of disorder is small. Consequently, we may anticipate a relation between stress and strain near the melting

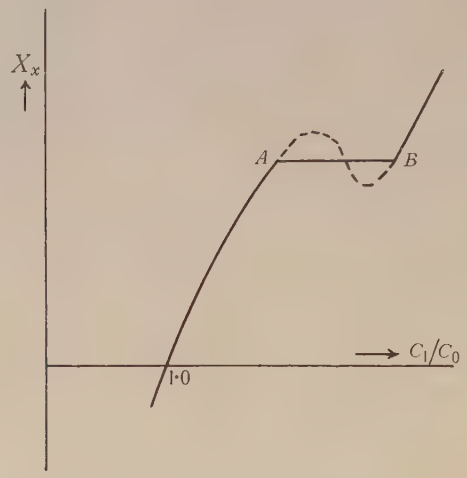

Figure 4. The relation between stress and strain for a perfect crystal subject to large stresses.

point somewhat like that shown in figure 4. The setting-in of disorder produces a diminution in the stress between the points marked A and B. Moreover, if the stresses are such as to maintain c_2 and c_3 constant, then the system will follow the straight-line path from A to B, in analogy with melting at a constant pressure, and this indicates a yield of the crystal at that particular stress. It is to be expected, however, that the magnitude of the stress in question will be a sensitive function of temperature, and that its value will be extremely high for temperatures removed by more than a few degrees from the melting point.

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DISCUSSION. PART I

Prof. W. L. Bragg. In view of Dr Burgers's paper, it may be worth while to specify rather more closely certain properties of the interfaces between two crystallites with different orientations. A two-dimensional picture of such an interface is shown in figure 1. The crystalline arrangement is shown as being perfect on either

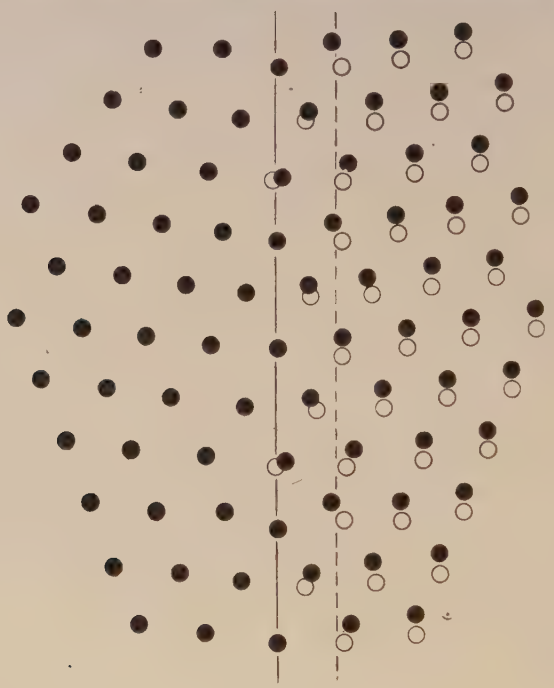

Figure 1.

side of the vertical lines. The intermediate atoms which are in a position of compromise between the two structures have been so placed that the interatomic distances remain approximately constant, and it is remarkable how closely this can be achieved. Furthermore, it is interesting to note that the structure on the right can slip relatively to that on the left by means of very slight displacements of the atoms. If the boundary moves from the full line to the dotted line, certain atoms join the scheme of structure on the left-hand side, and corresponding atoms leave the structure on the left-hand side to take up irregular positions. The black circles become the open circles. In this way the whole structure on the right moves relatively to that on the left without any large displacement of any one atom at the boundary. The boundary may be regarded as a series of Taylor dislocations in which an extra atom is introduced at every nth row into the nearly horizontal rows as one goes downwards. It differs from Taylor's picture in that the dis-

dislocations are spaced regularly over a sheet, the intercrystalline boundary. This makes it possible for slip to take place without any local violent shift of atoms such as would be necessary if a single dislocation ran over a crystallographic plane. It is to be noted that the type of shear shown in the figure, when one block moves downwards relatively to the other, is in actual fact equivalent to a shear from right to left along the rows, the difference being merely a rotation of the composite crystal as a whole. It is suggested that slip consists in the creation and movement of such faults or boundaries in the initially perfect crystalline structure. The unit of dislocation, in other words, is a boundary between two crystallites with different orientations, not a point where an atom is missing or even a line along which a whole row of atoms drops out. This idea is supported both by the lineage structure of real crystals demonstrated by Buerger, and by the fact that x rays show slip to be characterized by the appearance of crystallites making angles with each other.

Dr W. A. Wooster. The mechanism of gliding which Prof. Bragg has suggested differs from that proposed by G. I. Taylor[1] and Orowan in that whole planes, instead of lines of atoms, slip into new positions simultaneously. Such a mechanism may be expected to occur in glide twinning. For instance, in calcite a glide twin may be produced by pressing a knife-blade into a rhomb of the crystal at right angles to any polar edge. The twinned portion has optically perfect faces and its x-ray reflexions are sharp. In the process of glide twinning the crystal does not appear to remain in any orientation intermediate between the initial and final state. We may therefore suppose that the twin is built up by one plane after another switching over to a new orientation.

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Dr W. G. Burgers. With regard to the importance of the glide direction in the process of gliding, it seems worth mentioning[1] that in experiments with rectangular blocks of rocksalt crystals, it was found that, for two equivalent glide planes for which the shear stress was the same, gliding took place along that plane for which the length of the glide direction in the crystal was shortest.

Attention may also be drawn to recent papers[2]–[4] in which the occurrence in deformed single-crystal and polycrystalline test pieces of aluminium, iron, and β brass of so-called deformation bands together with normal glide lines is observed and discussed. The exact meaning of the deformation bands seems not yet to be perfectly clear, but they play, according to the authors, an important rôle in the deformation process. They occupy larger regions in the crystals, gliding taking place along different glide combinations in adjoining bands. Thus different parts of the same crystal rotate, as a result of the gliding, in different directions. Barrett suggests that the asterism in the Laue photographs of deformed crystals, which is usually connected with rotations of parts of the glide lamellae or glide packets

(see Prof. Andrade's paper) may be connected with the occurrence of the deformation bands.

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Prof. N. F. Mott. From the preceding papers and the discussion which followed, it may be useful to summarize some of the points of view expressed.

Two mechanisms of slip have been suggested—the dislocation theory of G. I. Taylor, Orowan and others (this volume), and the alternative mechanism suggested by Bragg above. At present it appears uncertain which is the correct mechanism, or whether both take place in different cases.* Theories based on the dislocation hypothesis have been developed further, and will be discussed here.

The dislocation theory pictures the perfect crystal as an elastic medium, having no plastic properties and having the theoretical yield point; i.e. glide should not take place until the crystal is sheared through an angle of the order of ten to thirty degrees. If the crystal contains any dislocations (and in practice it always does), it will have a very much lower yield point, because the dislocations can move easily through the crystal.

The rate at which a crystal will yield under stress, i.e. the creep rate, may be determined, as has been emphasized by Orowan, (1) by the rate at which new dislocations are formed, and (2) by the rate at which they move under the external stress. Orowan believes that usually (2) is the determining factor, and also that the yield point is the stress required to move the dislocations at an observable rate.

As regards the origin of the dislocations, it is believed that they are formed at special spots in the crystal where the stress is particularly high. Thus irregularities in the crystal have two rôles—to make possible the formation of dislocations, and to hinder their motion. If (1) determines the resistance to glide, irregularities may soften the material, while if (2) determines it, irregularities may harden the material. Orowan gives evidence to show that both cases may occur in practice.

It was suggested that glide starts by the formation and motion in a given crystallographic direction of a dislocation of atomic dimensions, but that as soon as the stress had reached the point at which a dislocation could move at all rapidly† the heat developed would cause the formation of a dislocation of a much larger order of magnitude, giving the macroscopic slip bands observed.

As regards the factors resisting the motion of a dislocation, Peierls's paper shows that a finite stress is required to move a dislocation even in a perfect crystal; thus

* W. A. Wooster (this volume).
† When $(\sigma_d - \sigma)^2 V/2GkT \simeq 1$ in Orowan's formula (7).

in contradiction to G. I. Taylor's hypothesis) a perfect crystal containing just one dislocation should have a finite though small resistance to shear at a low enough temperature.

The much greater resistance to the motion of a dislocation in an age- or work-hardened material must be due to deviations from the ideal lattice. Two hypotheses are possible, (1) that the dislocations are stopped at surfaces of misfit between crystallites; and (2) that the motion of dislocations is impeded by the presence of internal strains.* If σ_i is the internal shear stress at any point in the lattice, the directions of σ_i will be random. Thus at some points along the length of a dislocation (i.e. along the line ABC in figure 3 of Orowan's paper) the dislocation will be pushed one way, while at other points it will be pushed another way. For the dislocation to move in a definite direction, the external stress σ must be greater than $|\sigma_i|$ at all points along the dislocations; thus the observed yield point should be of the order of the mean value of $|\sigma_i|$ (see the paper by Mott and Nabarro in this volume).

* G. I. Taylor's theory makes use of both hypotheses. The dislocations are supposed to be stopped by surfaces of misfit in the lattice, but this does not lead to any resistance to shear, because it is assumed that new dislocations can always be formed at surfaces. The hardening comes because the strain round the anchored dislocations prevents new dislocations from moving.

II. PRECIPITATION IN METALS AND AGE-HARDENING

SOME ASPECTS OF DIFFUSION IN SOLIDS

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ABSTRACT. This paper summarizes and discusses data on diffusion constants in ionic and metallic systems in terms of the equation $D=D_0e^{-E/RT}$. Theories of diffusion are outlined, and expressions for the diffusion constant together with the relationship of the diffusion constant to other physical quantities are considered. Similarities between diffusion and chemical reaction are brought out by considering the entropy of activation and periodicity curves for D_0.

§ 1. INTRODUCTION

The study of diffusion probably began with early attempts to carburize steel. The velocity with which this interdiffusion can occur was not realized until Roberts-Austen[1] (1896) showed that at 500° C. gold will diffuse through lead faster than sodium chloride will diffuse through water at 18° C. It is possible to siphon mercury through a bent lead strip, in which the mercury dissolves and diffuses. Numerous processes of alloy formation, homogenizing, and the formation of veneer metals and bimetal strip[2] illustrate the technical importance of the interdiffusion of solids. Diffusion limits the velocity of reaction of many chemical processes involving solids, for example, the oxidation velocities[3] of iron, nickel, copper and brass. Not only is the technique of measuring the concentration gradients of two interdiffusing solids often troublesome, but also the interpretation of the results may be extremely difficult when the concentration gradients have been established. It has hitherto been customary to employ various integrated forms of the Fick diffusion law

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2},$$

where D is the diffusion constant, c the concentration, x the co-ordinate along which diffusion proceeds, and t the time. However, the interpretation of even the simplest concentration gradients may not be satisfactory when the above law is used. It has been shown[4, 5] that D is usually a function of c, so that the law to be employed is

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right).$$

As far as the interpretation of diffusion data is concerned, the most important advance is the Matano method of using this equation to determine D. Matano expressed the law in the form

$$D_{c=c_1}=\frac{1}{2t}\frac{dx}{dc}\int_{c_1}^{c_0}x\,dc, \quad \text{where} \quad \int_0^{c_0}x\,dc=0,$$

in which form it may be solved graphically, since dc/dx can be calculated from the experimental curves of the concentration as a function of distance.

In all systems to which the Matano method of analysis has been applied it has been found that D is a function of concentration, figure 1. D may be expressed by

$$D = D_0 e^{-E/RT},$$

where D_0 and E are characteristic constants. E is variously called the "energy of activation for diffusion", the "Auflösungsarbeit", or the "Auflockerungsenergie".

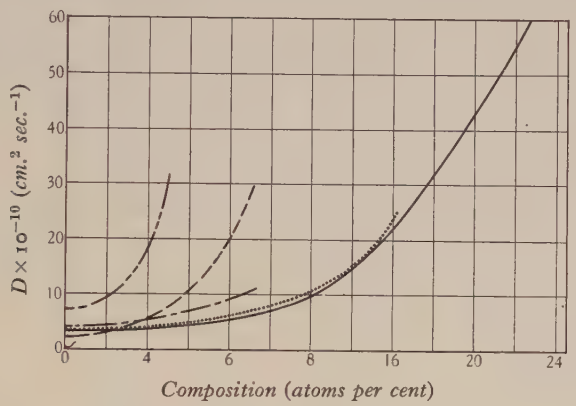

Figure 1. Diffusion constant as a function of composition for copper alloys (Rhines and Mehl) at 800° C. Al .....; Be — — —; Si — — — —; Sn — — — —; Zn ———.

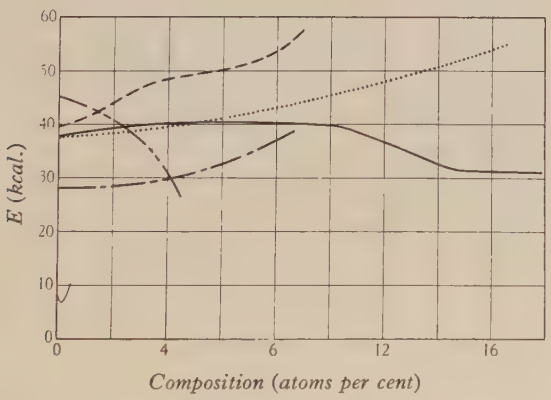

Figure 2. Influence of composition on activation energy E (kcal.). Al .....; Be — — —; Si — — — —; Sn — — — —; Zn ———.

The latter two terms suggest that diffusion follows a local loosening of the lattice which occurs after an activation energy has been supplied. This activation energy E is also a function of the concentration, figure 2. These results indicate that in many diffusion systems to which the simple Fick law ($\partial c/\partial t = D\,\partial^2 c/\partial x^2$) has been applied, the calculated values of D and E are an average only over a limited range of compositions.

Table 1. Diffusion constants of ions in salts according to the equation $D = D_0 e^{-E/RT}$

System	D_0 (cm²/sec.)	E (kcal. per ion)	E (kcal. per ion) from Langmuir-Dushman formula
Group I. Salts for which $E > 10{,}000$ kcal. per ion			
Ag^+ in AgCl	—	23,000	19,300
Ag^+ in AgBr	—	19,000	21,000
Na^+ in NaCl	—	11,800	35,000
Cl^- in NaCl	—	47,200	38,600
Pb^{++} in $PbCl_2$	7·7	35,800	34,500
Pb^{++} in PbI_2	4·9, 10·6	30,000	29,000
Cl^- in $PbCl_2$	—	11,000	18,000
Se'' in α-Ag_2S	67×10^{-5}	20,040	—
Ag^+ in α-Cu_2Te	2·4	20,860	—
Group II. Salts for which $E < 10{,}000$ kcal. per ion			
I' in PbI_2	—	9,300	4,300
Ag^+ in α-CuI	$4{\cdot}5 \times 10^{-3}$	6,760	—
Li^+ in α-AgI	$58{\cdot}3 \times 10^{-4}$	4,570	—
Cu^+ in α-AgI	$16{\cdot}3 \times 10^{-5}$	2,260	—
Cu^+ in α-Ag_2S	46×10^{-5}	3,180	—
Cu^+ in α-Ag_2Se	$15{\cdot}5 \times 10^{-5}$	2,940	—
Cu^+ in α-Ag_2Te	$3{\cdot}85 \times 10^{-5}$	2,660	—
Ag^+ in α-Cu_2S	$32{\cdot}7 \times 10^{-5}$	4,570	—
Ag^+ in α-AgI	—	2,260	—

In tables 1 and 2[6, 5, 7] are collected values for the constants D_0 and E in the equation $D = D_0 e^{-E/RT}$ for many salt- and metal-diffusion systems. In table 2, systems which may show structure-sensitive diffusion are marked thus †. It is found that structure-sensitive diffusion occurs in hard metals (bismuth, tungsten), in which mechanical working and strains create faults through the crystal. Soft metals such as lead do not show structure-sensitive diffusion, because diffusion through the lattice occurs much more readily (i.e. with a smaller activation energy), and the metal does not so readily develop grain boundaries. The activation energy decreases in the order

E (lattice diffusion) > E (grain-boundary diffusion) > E (surface diffusion),

the corresponding equations for the diffusion of thorium on and in tungsten being

Surface diffusion, $D = 0{\cdot}43 e^{-66{,}000/RT}$.

Grain boundary diffusion, $D = 0{\cdot}75 e^{-94{,}000/RT}$ (small grains).

Lattice diffusion, $D = 1{\cdot}0 e^{-120{,}000/RT}$.

It is also to be noted that the values of D_0 in tables 1 and 2 are greatest for self-diffusion, or for diffusion between chemically and physically similar metals, which may often give a continuous series of solid solution; such systems are marked * in table 2. This rule is invariable for self-diffusion, but not without exceptions for systems of 100 per cent mutual solubility (e.g. palladium in gold, silver in gold). It will later be indicated how this rule can be interpreted in terms of Eyring's theory of diffusion (table 6).

Table 2. Diffusion constants in metals according to the equation $D = D_0 e^{-E/RT}$

System	D_0 (cm²/sec.)	E (kcal. per atom)	E (kcal. per atom) from Langmuir-Dushman formula
*Pb in Pb	5·1	27,900	24,400
β-Tl in Pb	$3·7 \times 10^{-2}$	21,000	22,400
β-Sn in Pb	$3·4 \times 10^{-1}$	24,000	23,200
Au in Pb	$4·9 \times 10^{-1}$	13,000	13,300
Ag in Pb	$7·5 \times 10^{-2}$	15,200	—
Bi in Pb	$7·7 \times 10^{-3}$	18,600	21,900
Hg in Pb	$3·6 \times 10^{-1}$	19,000	—
Cd in Pb	$\sim 2·1 \times 10^{-2}$	~18,000	20,000
Zn (9·58 %) in Cu	$3·2 \times 10^{-2}$	42,000	41,000
Zn (29·08 %) in Cu	$5·8 \times 10^{-3}$	42,000	38,000
Sn (10 %) in Cu	—	40,200	40,000
*Au in Au	$1·26 \times 10^{2}$	51,000	—
*Pd in Au	$1·11 \times 10^{-3}$	37,400	—
*Cu in Au	$5·8 \times 10^{-4}$	27,400	—
*Pt in Au	$1·24 \times 10^{-3}$	39,000	—
†Th in W (small grains)	$7·5 \times 10^{-1}$	94,000	96,700
†Th in W (large grains)	$4·1 \times 10^{-3}$	94,400	118,200
Th in W (volume)	1·0	120,000	—
†U in W	1·0	100,000	100,500
†Yt in W	0·46	68,000	70,100
†Ce in W	1·0	83,000	82,700
†Zr in W	1·0	78,000	77,400
†*Mo in W (polycryst.)	5×10^{-3}	80,500	—
*Mo in W (single cryst.)	$6·3 \times 10^{-4}$	80,500	—
N_2 in Fe	$1·07 \times 10^{-1}$	34,000	38,100
C in Fe	$4·9 \times 10^{-1}$	36,600	36,700
†C in W_2C	—	108,000	—
Zn in (Cu + 4 % Zn)	$1·57 \times 10^{-3}$	34,100	—
Al in (Cu + 4 % Al)	$6·34 \times 10^{-2}$	40,400	—
Si in (Cu + 4 % Si)	$1·0 \times 10^{4}$	64,200	—
Sn in (Cu + 4 % Sn)	$6·7 \times 10^{2}$	54,000	—
*Cu in Ni	$1·04 \times 10^{-3}$	35,500	—
Cu in Ag	$5·9 \times 10^{-5}$	24,800	—
Sb in Ag	$5·3 \times 10^{-5}$	21,700	—
Sn in Ag	$7·9 \times 10^{-5}$	21,400	—
In in Ag	$7·3 \times 10^{-5}$	24,400	—
Cd in Ag	$4·9 \times 10^{-5}$	22,350	—
*Au in Ag	$1·1 \times 10^{-4}$, $5·3 \times 10^{-4}$	26,600, 29,800	—
*Pd in Ag	$4·16 \times 10^{-6}$	20,200	—
Au in Ag-Au	$5·2 \times 10^{-4}$	29,800	—
Ag-Pd (20 % Pd) in Ag-Au	$7·0 \times 10^{-6}$	20,200	—
Au-Pd in Ag-Au	$8·3 \times 10^{-4}$	37,400	—
Cu in Ag-Au	$1·06 \times 10^{-3}$	27,400	—
Au-Pt in Ag-Au	$1·28 \times 10^{-3}$	39,000	—
†Bi in Bi ($\perp$ c-axis)	$1·16 \times 10^{49}$	145,000	—
†Bi in Bi ($\parallel$ c-axis)	$2·2 \times 10^{-4}$ to 6×10^{-4}	30,000	—
Cu in Al	2·3	34,900	31,400
Mg in Al	$1·5 \times 10^{2}$	38,500	29,000
Al in Cu	$1·2 \times 10^{-2}$	37,500	—
Zn in Cu	8×10^{-1}	38,000	44,000
Sn in Cu	1·0	45,000	—
Si in Cu	$5·2 \times 10^{-2}$	39,950	—
Be in Cu	$4·5 \times 10^{-5}$	27,900	—
Cd in Cu	$3·5 \times 10^{-9}$	8,200	—
Zn in (Cu + 20 % Zn)	—	31,000	38,500
Al in (Cu + 16 % Al)	—	54,000	39,000

* Interdiffusing metals form a continuous series of solid solutions.
† Diffusion may show structure-sensitivity.

The data on salt systems show that on the average the energy needed to render an ion mobile in an ionic lattice is smaller than the energy needed for diffusion in a metallic lattice. There are many ionic diffusion systems wherein the activation energy is very small indeed, and the diffusion rates are exceptionally high. In these systems one ion at least is readily polarizable, so that the polarization energy reduces the energy needed to remove the ion to an interstitial lattice position or to create a vacant lattice site. Silver iodide and Ag_2HgI_4 are extreme examples of disordered lattices, for there is in these salts an almost complete cation disorder[9, 10] in an ordered anionic lattice. The conductivity of some salts of this kind may exceed that of the molten crystal (e.g. α-CuBr[11]).

§ 2. DEPENDENCE OF *D* ON SOME CRYSTAL PROPERTIES

(*a*) *Ionic or atomic radii.* Lehfeld[12] showed that the energy E in the equation $K = Ae^{-E/RT}$ for the conductivity of a salt depended upon the radius of the halogen ions to a considerable degree, figure 3.

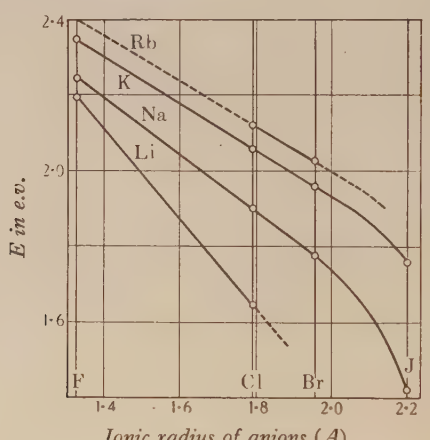

Figure 3. Dependence of E, in the conductivity equation $K = Ae^{-E/RT}$, upon ionic radius (Lehfeld).

Disparity in atomic or ionic radii determines the type of disorder in an ionic lattice. When the ions are of similar radii the disorder in the lattice consists of vacant sites in equilibrium with occupied sites, but there are no interstitial ions, since the interstitial spaces are not large enough to accommodate either species. When the ions are of very different radii, the ion of smaller radius may exist in interstitial positions. Thus diffusion may be predominantly of vacant lattice sites, or of interstitial ions in the two instances. In a metallic lattice, a large disparity between atomic radii of solvent and solute may indicate that diffusion will be zeolitic in type, i.e. the smaller atom penetrates down the interstitial channels, and diffusion need not occur by change of place.

Sen[13] indicated another relationship between atomic radii and speed of diffusion. If there are two metals M and N, the most rapid diffusion is that of M

into N when the closest distance of approach of the atoms N in the crystal is greater than the same distance in M, table 3.

Table 3. Effect of atomic radius upon direction of diffusion

System	Minimum distance of approach (cm.)		Direction of most rapid diffusion
Cu-Pt	Cu: $2{\cdot}54 \times 10^{-8}$	Pt: $2{\cdot}78 \times 10^{-8}$	Cu into Pt
Cu-Zn	Cu: $2{\cdot}54 \times 10^{-8}$	Zn: $2{\cdot}67 \times 10^{-8}$ $2{\cdot}92 \times 10^{-8}$	Cu into Zn
Fe-Ag	Fe: $2{\cdot}54 \times 10^{-8}$	Ag: $2{\cdot}876 \times 10^{-8}$	Fe into Ag
Au-Pb	Au: $2{\cdot}88 \times 10^{-8}$	Pb: $3{\cdot}48 \times 10^{-8}$	Au into Pb
Fe-C	Fe: $2{\cdot}54 \times 10^{-8}$	C: $1{\cdot}50 \times 10^{-8}$	C into Fe

(*b*) *Polarization effects.* Polarization may occur in a metallic lattice, although it is not easy to demonstrate polarization of the atoms in metals. However, when gold is dissolved in lead, palladium or copper, or carbon in iron, the solid solutions obtained may be electrolysed, which indicates polarization of the components [14]. Polarization is a maximum when the *electron affinity* of one constituent is large and of the other constituent small. Figure 4, due to v. Hevesy [15], shows the mobility of

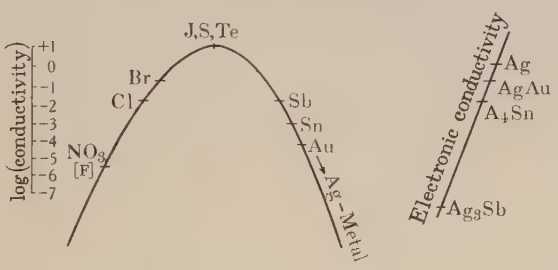

Figure 4. The mobilities of silver ions in silver compounds and alloys arranged in a parabola. On the right is the electronic conductivity.

silver in a number of ionic and metallic lattices arranged around a parabola. It is seen that ionic mobility rises strongly with electron affinity. The right-hand side shows how the small self-diffusion rate of silver in silver is raised by additions of the metals tin or antimony, while the electronic conductivity diminishes.

(*c*) *Melting point.* As a qualitative measure of the extent of the lattice-loosening existing in a crystal, v. Hevesy [15] suggests that one might employ the ratio

$$\frac{\text{conductivity above the melting point}}{\text{conductivity below the melting point}}.$$

Usually there is a great discontinuity in conductivity at the melting point, but, as table 4 shows in a few cases, the ions carrying the current may be just as numerous and mobile in the solid as in the melt. Another method of comparing the relative loosening in two lattices is to measure the ratio

$$\frac{\text{self-diffusion constant for first metal}}{\text{self-diffusion constant for second metal}}.$$

This ratio for lead and gold at 326° C. is 26,000, so that one would say the lead lattice is extensively loosened at this temperature, but the gold lattice is not.

Table 4. The ratio of conductivities above and below the melting point

System	Ag^+ in AgCl	Ag^+ in AgBr	Ag^+ in AgI	Li^+ in LiCl	Na^+ in NaCl	Na^+ in $NaNO_3$
Mobility ratio above and below melting point	16	2·5	0·5	$1·0 \times 10^4$	$1·5 \times 10^5$	$1·0 \times 10^5$

The relation between diffusion velocity and the melting point has been recognized for some time. Braune[16], and van Liempt[17] (see table 6), attempted to incorporate the relationship in diffusion formulae in which the exponential term E/RT in the equation

$$D = D_0\, e^{-E/RT}$$

was written thus:

$$\frac{E}{RT} = 3b^2 \frac{T_m}{T},$$

where T_m is the melting temperature of the solvent. In these equations the usual value of b^2 is about 1 or 2. For the lattices of lead, silver and tungsten, of very different melting points, the values of b^2 are as 1 : 2 : 1 while the melting temperatures are as 1 : 3 : 10. Table 5 shows the relation between E and T_m for several diffusion systems.

Table 5

System	Cu in Au	Cu in Ni	Mo in W
T_m (° K.) (solvent metal)	1356	1728	3473
E/T_m	20·2	20·6	21·3

(*d*) *Connexion with order-disorder transformation in alloys*[18]. When a binary alloy with constituents in the ratio 1 : 1 or 1 : 3 is cooled, the melt first solidifies to give a crystal. In this crystal a given lattice point is as likely to be occupied by an atom of the first kind as of the second. As the lattice is cooled a reorganization may occur at a fairly definite temperature, in which certain lattice sites are always occupied by one kind of atom and other sites by the other kind of atom. The type of atomic jump occurring in this reorganization process may be closely allied with the jumps occurring in diffusion. Unfortunately the disorder-order transformation occurs in a series of small zones throughout the crystal, which are out of phase with one another. The transformation to complete order occurs only by a secondary slow swallowing-up of one zone by another. In each separate zone, however, the time τ required for the transformation should be given by

$$\tau = Ae^{-E/RT},$$

where A is a constant and E is an energy of activation. It would be interesting to have data comparing E in the equations

$$\tau = Ae^{-E/RT}$$

and

$$D = D_0\, e^{-E_1/RT}.$$

§ 3. THEORETICAL TREATMENTS OF DIFFUSION

There has been considerable discussion as to how diffusion takes place in a solid. When the interstices are large and the diffusing molecule small, diffusion tends to be zeolitic in type, occurring down interstitial channels. Examples of zeolitic diffusion are given below:

H_2, He, Ar in SiO_2 glass[19].
NH_3, H_2O in zeolites[20].
H_2 in Pd[21].
Au in Pb (v. Hevesy[15]).*

A kinetic theory of hydrogen diffusion in palladium and of gases or vapours in zeolites was given by Hey[20, 21]. It is probable that amalgamation is also zeolitic in type, but accompanied simultaneously by a disintegration or reorganization of the solvent lattice into amalgams.

Diffusion may also occur by place-exchange in the lattice, i.e. a process in which, after a local melting in the lattice brought about by the supplying of an activation energy, a pair of atoms, one solute and one solvent, change places. Bernal[22] indicated how a place-change could occur by a series of localized processes of shear, occurring spontaneously. Another suggestion is that place-change takes place when there exist in a metallic or ionic lattice a number of vacant sites or interstitial atoms or ions, which at high temperatures are in thermodynamic equilibrium with the ordered lattice. If the interstitial volume is too small to hold a displaced atom, the disorder will tend to consist only of vacant lattice sites. Diffusion is then possible as a drift of vacant sites down a concentration gradient. These viewpoints have been developed extensively by Wagner[23], Jost[6, 24] and the German school, principally for ionic lattices. The different types of disorder have been investigated experimentally as well as theoretically, and in a few instances energies of disorder have been measured. These energies for the formation of vacant sites and interstitial silver ions in silver halide lattices are as follows:

AgCl: $E \simeq 25{,}000$ cal. per ion,
AgBr: $E \simeq 20{,}200$ cal. per ion.

Frenkel[25], and later Jost[26], developed a theory of conductivity in ionic crystals based upon the concept of an equilibrium state of disorder in a crystal. By applying Einstein's law† to the movements of ions in crystals, various workers have related conductivity and diffusion constants.

On the Frenkel[25] theory (table 6) the value of the conductivity k should be given by

$$k \simeq (10 - 100)\, e^{-E/RT},$$

* Although v. Hevesy regards this diffusion as zeolitic, the disparity in the radii of Au and Pb atoms (2·88 A. and 3·48 A. respectively) does not seem sufficient for gold to form a truly interstitial solution in lead.

† $D = BkT$, where B denotes the mobility of the ion, D its diffusion constant, k the Boltzmann constant, and T the temperature (° K.).

where the energy term is composed of the energy needed to create a vacant site and interstitial ion, and the energy needed for the diffusion of interstitial ions (or vacant sites). It might at first sight be thought that E would be of the order of the lattice energy (100 to 200 kcal.), while experiment gives E as being from 1 to 50 kcal. However, when the polarization energy is taken into account, the experimental and theoretical values are of the same order of magnitude[26], as is indicated below:

Salt ...	NaCl	α-Ag_2S
$E_{calc.}$	57,000	13,100
$E_{exp.}$	44,000	3,220

Other expressions for the diffusion constant have been based upon kinetic theory and upon models of the crystal lattice indicated by x-ray crystallography. One of the earliest of these was due to Langmuir and Dushman. Their equation was semi-empirical, and gave

$$D = \frac{E}{Nh} d^2 e^{-E/RT},$$

where E denotes the energy of activation, d the lattice parameter (equated to the mean free path), and h is Planck's constant. This equation has had extensive application to diffusion systems, and represents the experimental data extremely well in many instances. The comparison between $E_{calc.}$ and $E_{exp.}$, the Langmuir-Dushman[27] equation being used to determine $E_{calc.}$, is given in tables 1 and 2. The equation is inaccurate when the activation energy is small, and when grain-boundary processes occur.

With the same assumptions as those used by Langmuir and Dushman, a more accurate derivation leads to the equation[28]

$$D = \tfrac{1}{6} \nu d^2 e^{-E/RT},$$

where ν is the vibration frequency. This equation corresponds to a communication of the activation energy in only one degree of freedom. When two degrees of freedom or f degrees of freedom are involved, the equations are respectively[29, 30]

$$D = \frac{1}{6} \frac{E}{RT} \nu d^2 e^{-E/RT},$$

$$D = \frac{1}{6} \left(\frac{E}{RT}\right)^{(f-1)} \frac{1}{(f-1)!} \nu d^2 e^{-E/RT}.$$

Barrer[28] showed that when diffusion occurs in elastic polymers 12 or 14 degrees of freedom must be considered, corresponding to the "fast" reactions of chemical kinetics.

Cichocki[31] recently calculated the diffusion constant in a crystal by computing the probability that a given atom would have the requisite energy and direction of vibration to move to a new position at a time at which the atoms surrounding that position have the energy and direction of vibration to make an adequate interstice for it. His theory is interesting as an attempt to allow for correct timing in the diffusion. An analogous treatment by Dorn and Harder[32] seems less satisfactory.

Table 6. Expressions for the diffusion constant and the ionic conductivity in crystals

System	Formula	Author
Ion-ionic lattice metal atom, metallic lattice	$D=\frac{d\bar{v}}{2}e^{-(E_0+2E_1)/RT}$	Frenkel[25], Jost[26]
	d, mean free path; E_0, energy of hole formation in the lattice; E_1, activation energy for diffusion of ion or atom into hole; $\bar{v}$, mean thermal velocity of diffusing atom or ion	
	$K_{\text{ionic crystal}}=N(Ze)^2 D/KT$	Ditto
	K, conductivity; Z, valence; e, electronic charge; N, Avogadro's number	
Ionic or metallic lattice	$D=\frac{E}{Nh}d^2e^{-E/RT}$	Langmuir and Dushman[27]
	$D=D_0e^{-3b^2T_m/T}$	Braune[16]
	$D=\frac{8}{3\pi}\nu d^2e^{-3b^2T_m/T}$	Van Liempt[17]
	b, a constant between 1 and 2; T_m, melting temperature; ν, vibration frequency of the solute in the solvent lattice; R, Planck's constant; d, mean free path, equated to the lattice parameter	
Ionic lattice	$K=\frac{1}{d}\frac{2e^2}{3\tau(8\cdot3)}\frac{N}{E}e^{-E/RT}$	Braunbeck[35]
	E, activation energy for ion transfer; τ, vibration period, about 2×10^{-13} sec.	
Metallic or ionic lattice (self-diffusion)	$D=2\cdot43\times10^3\frac{M}{V}\sqrt{\frac{T_m}{M}}e^{-(E_1+E)/RT}$	Cichocki[31]
	V, molecular volume; T_m, melting point; E_1, energy needed to make a hole; E, energy needed to bring an atom into it	
Ionic or metallic lattice	$D=\frac{1}{6}\nu\left(\frac{E}{RT}\right)d^2e^{-E/RT}$	Bradley[29]
	$D=\frac{1}{6}\left(\frac{E}{RT}\right)^{(f-1)}\frac{\nu d^2}{(f-1)!}e^{-E/RT}$	Wheeler[30]
Ionic or metallic lattice	$D=\frac{kT}{h}\Big/\alpha\frac{F_a^*}{Fn}d^2e^{-E/RT}$	Eyring[33]
	F_a^*/Fn, ratio of partition functions of transition and normal states respectively (excluding for former the partition function for co-ordinate in which diffusion process occurs); α, transmission coefficient, i.e. probability that when system reaches transition state it passes over to a *new* initial state	
	$D=e^{\Delta S\pm/R}\left(\frac{kT}{h}\right)d^2e^{-\Delta H\pm/RT}$	Eyring and Wynne-Jones[34]
	$\Delta S\pm$, $\Delta H\pm$, entropy and heat of activation	

In 1936 Eyring[33] showed how the transition-state theory of reaction velocity could be applied to diffusion in liquids. Like the theories of Bradley and of Wheeler, which were also derived for liquids (table 6), there is no reason why Eyring's theory should not apply more appositely to diffusion in crystals. Eyring and Wynne-Jones[34] used the concept of entropy of activation ($\Delta S\pm$) and heat of activation ($\Delta H\pm$) in dealing with reaction velocities, and this model may again be carried over to the diffusion process in solids. In table 6 are given the different equations which have been derived in treating the process of diffusion. It may there be seen what concepts have been correlated with diffusion.

§ 4. THE ENTROPY OF ACTIVATION IN DIFFUSION PROCESSES

When one compares the equations

$$D = D_0 e^{-E/RT}$$

and

$$D = e^{\Delta S\pm/R}\left(\frac{kT}{h}\right) d^2 e^{-\Delta H\pm/RT},$$

it is found that

$$D_0 = e^{\Delta S\pm/R}\left(\frac{kT}{h}\right) d^2 \frac{1}{2{\cdot}72}.$$

Thus systems in which D_0 has a large value are systems with a large entropy of activation; for instance, self-diffusion processes (tables 1 and 2), and diffusion in elastic polymers[28], figure 5. The large entropy of activation corresponds to the storing of activation energy in many degrees of freedom, that is, to a large increase in the disorder of the lattice on passing from the initial to the activated state. It is interesting to inquire why in self-diffusion a large entropy of activation is observed. One possibility is that the more similar the solute and solvent atoms are, the more readily the solute becomes a part of the solvent lattice, without loosening it and so increasing its entropy. The more dissimilar solute and solvent atoms are, the more the solvent lattice is loosened, and the greater the entropy of solution. Thus the increase in disorder in passing from the initial dissolved to the activated state is less in the latter case than in the former, and so the value of $\Delta S\pm$ or D_0 is correspondingly smaller.

The range of values of D_0 was compared by Barrer[28] with the range of values of k_0 for unimolecular reaction velocities. Figure 5 shows log D_0 (proportional to $\Delta S\pm$) plotted against the number of diffusion systems for which D_0 lies within certain limits. The full curve gives the mean periodicity curve for a large number of diffusion processes in rubbers, liquids, and ionic and metallic solids, and on surfaces. The dotted curves are respectively for rubbers, for liquids, and for crystals, metals and glasses. It is apparent that diffusion in elastic polymers occurs with a large entropy of activation, while in liquids and in solids the activation process usually occurs with a smaller entropy of activation (i.e. fewer degrees of freedom are involved). The width of the band corresponds to a 10^8-fold range in D_0, and the greatest range in D_0 occurs in solid diffusion systems. This is probably

because in solids the greatest variety of structures appears, while rubbers and liquids approximate to single types with only minor structural singularities.

The values of D_0 in the equation $d = D_0 e^{-E/RT}$, and of k_0 in the equation $k = k_0 e^{-E/RT}$, where k is the first-order reaction-velocity constant, are related according to Eyring's theory by the expression

$$D_0 = d^2 k_0,$$

where d is the mean free path in the activated state. This may be assumed to be of molecular dimensions in most solids or liquids, and so the periodicity curve for

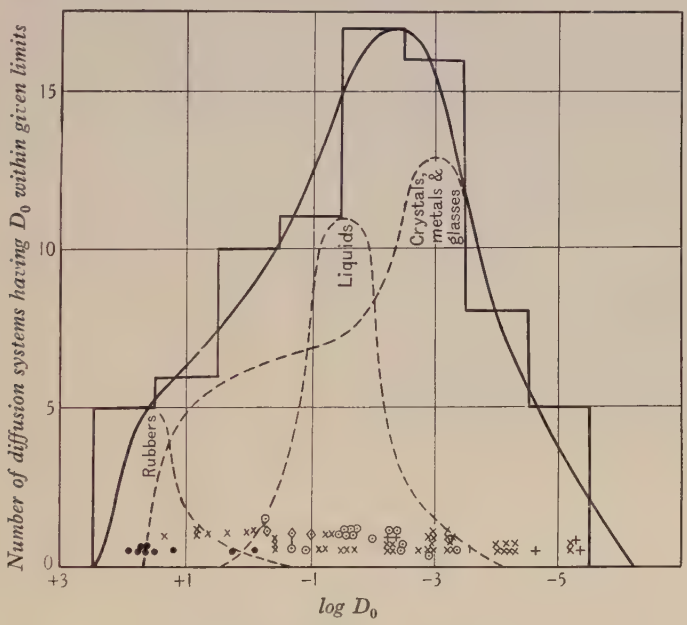

Figure. 5. Periodicity curve for D_0 in $D = D_0 e^{-E/RT}$. ● Rubber; × crystals; + glasses; ⊙ liquids; ◈ surface diffusions.

D_0, figure 5, may be compared with the analogous periodicity curve for k_0[36]. The spread in the latter case is 10^{13}-fold, and the maximum in the curve occurs at

$$k_0 \sim 10^{13-14} \text{ sec.}^{-1}.$$

In the diffusion systems the maxima were as follows

$$\text{rubbers: } k_0 \simeq 3 \times 10^{16} \text{ sec.}^{-1},$$
$$\text{liquids: } k_0 \simeq 3 \times 10^{13} \text{ sec.}^{-1},$$
$$\text{crystals: } k_0 \simeq 10^{12} \text{ sec.}^{-1}.$$

It is thus apparent that diffusion systems are in many respects comparable with systems undergoing chemical reactions.

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ON THE FORMATION OF NUCLEI DURING PRECIPITATION

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ABSTRACT. When an alloy in which precipitation is to take place is cooled, the process only begins with an observable velocity when the temperature has fallen by a definite amount below the temperature at which the single-phase alloy is in equilibrium. This fact is explained by a theory of nuclear formation. Also attempts may be made to calculate the rate at which nuclei form.

§ 1. INTRODUCTION

We consider the simplest case of a two-phase alloy consisting of two components A and B, as shown schematically in the phase diagram of figure 1, in which 100α denotes the concentration in atoms per cent of the component A. Single-phase alloys of both compositions are supposed to have

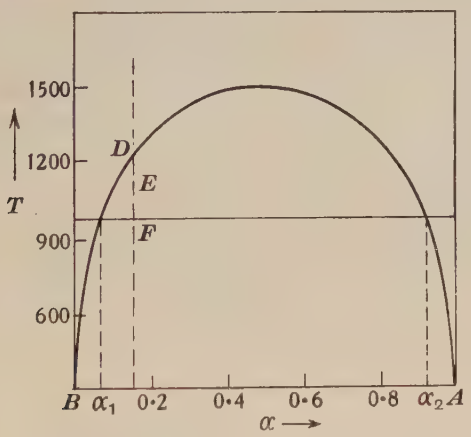

Figure 1. Phase diagram of a binary alloy capable of precipitation.

the same (cubic) crystal structure with the same lattice constant. If an alloy, rich in B, with the composition α is cooled below the equilibrium temperature D, let us say to the point F, then according to the predictions of thermodynamics it will separate into the two phases α_1 and α_2. It is known that this reaction actually takes place only very slowly if the temperature falls below D either by too little or by too much. The slowing-up of the reaction for very great supercooling can be understood at once. The process by which atoms change places is frozen up, so that no reaction which depends on place-changing can occur. The frequency with

which atoms change places depends on the temperature roughly through an activation energy Q, according to the formula $e^{-Q/RT}$.

The cause of the delay in the reaction at a temperature E, figure 1, just below the equilibrium line is quite different. Here there are two possible explanations[1], which depend on two different ways in which the separation of the two phases may be considered to take place. One of these was proposed by Borelius[2]. If we denote by $f(\alpha)$ the free energy of the alloy at a given temperature, a curve such as that shown in figure 2 will be obtained. The two compositions α_1 and α_2 which lie

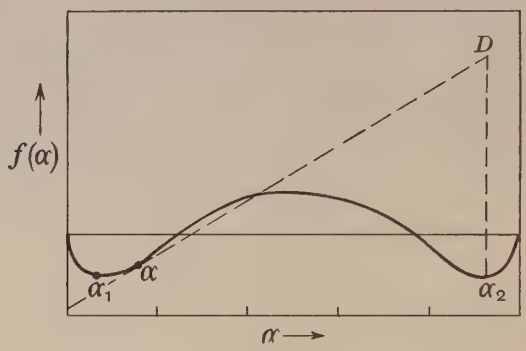

Figure 2. The free energy as a function of the composition for the temperature F of figure 1.

on the equilibrium curve are the points of contact of the common tangent to the $f(\alpha)$ curve. Between α_1 and α_2 are two points of inflexion. Homogeneous separation through a kind of negative diffusion which will increase small chance differences of concentration already existing can only take place between these two points. For if the concentration lies between α_1 and the neighbouring point of inflexion for instance, then for *small* differences of concentration we shall always have positive diffusion and so a smoothing-out of the differences.

Actually, however, in most practically important cases of precipitation hardening, the alloy is not yet in the region of negative diffusion. Therefore the precipitation cannot be considered as a continuous increase in small fluctuations of density, but can only take place if small regions of the alloy acquire the composition α_2, and grow through the diffusion of A atoms to them.

§ 2. CONDENSATION IN VAPOURS

This process is intimately connected with the formation of crystallites in supercooled melts, and also with the formation of drops in supersaturated vapours. Phase diagrams of the type shown in figure 1 cannot give us any information about this kind of process, because in the construction of the diagram it is assumed that the spacial arrangement of the phases is such that their surface energy is negligible in comparison with their volume energy. Actually, for a given degree of supersaturation, very small regions with the concentration α_2 are unstable when in contact with the homogeneous mixed crystal α. Instead of growing, they should dissolve again. Only when greater than a certain finite size can they act as nuclei for further

separation. We shall designate specially as a *nucleus* a region of composition α_2 of such a size that it remains in equilibrium with the supersaturated mixed crystal. This equilibrium is always unstable in the sense that any alteration in the size will lead either to the disappearance of the nucleus or to its further increase.

A similar question, the formation of drops in supersaturated vapours, has already been treated in a detailed and satisfactory way[3, 4]. If one denotes by p_r the vapour pressure of a droplet of radius r and correspondingly by p_∞ that of the liquid with a flat surface, then one obtains from thermodynamics

$$\boldsymbol{k}T \log \frac{p_r}{p_\infty} = \frac{m}{\rho} \frac{2\sigma}{r}. \qquad \text{.....(1)}$$

In this equation σ is the specific surface energy, m the mass of a molecule, and ρ the density of the liquid. In a supersaturated vapour, therefore, condensation cannot take place until a droplet has been formed of such a radius that its vapour pressure is equal to or less than that of the supersaturated vapour. Such a process is contrary to the second law of thermodynamics; it leads to an increase S in the entropy. According to Boltzmann the probability of such an event is proportional to $e^{-S/\boldsymbol{k}}$. In our case TS is equal to the work A which must be done in order to form a drop reversibly and isothermally in the middle of the supersaturated phase. A more exact calculation gives essentially for the number I of drops formed per second

$$I = Ke^{-A/\boldsymbol{k}T}, \qquad \text{.....(2)}$$

where K is the number of collisions per second between pairs of atoms. One can thus interpret $e^{-A/\boldsymbol{k}T}$ as the probability that any given collision leads to the formation of a drop. By putting numerical values in formula (2) one obtains satisfactory agreement with experiment for the degree of supersaturation at which spontaneous cloud-formation will take place.

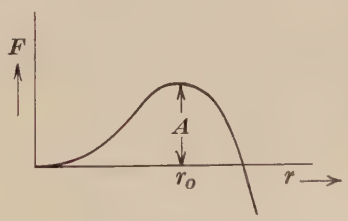

Figure 3. The energy F required for the reversible formation of a droplet of radius r in a supersaturated vapour.

We can obtain an expression for the energy A in the following way. We calculate first the energy F necessary to form a drop of arbitrary radius r. The quantity F is made up of a negative term proportional to the volume and hence to r^3, and a positive term proportional to the surface area and hence to r^2. Thus we may write

$$F = -\tfrac{4}{3}\pi r^3 \omega + 4\pi r^2 \sigma. \qquad \text{.....(3)}$$

In the case of condensation from a supersaturated vapour the gain in the energy is $\boldsymbol{k}T \log (p/p_\infty)$ per molecule, so that $\omega = (\rho/m)\, \boldsymbol{k}T \log (p/p_\infty)$. F is shown in figure 3 as a function of r. For small values of r the positive surface energy is

preponderant, for large values the negative volume part. In between there is a maximum. The height of this maximum is the required energy A for nuclear formation, and the radius r_0 at which the maximum occurs is the critical nuclear radius already given in formula (1). From the equation $(\partial F/\partial r)_{r=r_0}$ it follows that $A=4\pi\sigma r_0^2/3$, so that A is exactly a third of the surface energy of the critical drop.

§ 3. NUCLEAR FORMATION IN METALS

We have now to discuss the application of these ideas to precipitation in metals[6]. First we have to replace the number of gas-kinetic collisions by the frequency with which atoms change places. We thus obtain, for the number of nuclei capable of growing which are formed per second with the composition α_2,

$$I=Ce^{-Q/kT}e^{-A/kT}, \qquad \text{.....(4)}$$

where C is a constant. The numerical value of Q may be obtained from the temperature-dependence of the diffusion[5]. To calculate A we must consider both the terms which depend on the volume and those which depend on the surface. If we limit ourselves to nuclei having the form of cubes, with sides equal to a lattice constants, then we may write

$$F=-a^3\omega'+6a^2\sigma', \qquad \text{.....(5)}$$

where now the energies ω' and σ' refer to the energies of a single atom. If the curve $f(\alpha)$ of figure 2 is known, ω' can be given exactly. It is equal to the length α_2-D, where D denotes the point of intersection of the tangent at α to the curve $f(\alpha)$ and the vertical through α_2. If ω' and σ' are known, one obtains from (5)

$$\left(\frac{\partial F}{\partial a}\right)_{a=a_0}=0, \quad \text{or} \quad a_0=\frac{4\sigma'}{\omega'}, \qquad \text{.....(6)}$$

and

$$A=2a_0^2\sigma'=8\sigma'^3/\omega'^2.$$

For small degrees of supersaturation this formula can be developed further. If α is so near to α_1 that one can write approximately

$$f(\alpha)=f(\alpha_1)+\tfrac{1}{2}(\alpha-\alpha_1)^2 f''(\alpha_1),$$

then

$$\omega'=f''(\alpha_1)(\alpha-\alpha_1)(\alpha_2-\alpha)$$

and hence

$$A=\frac{1}{(\alpha-\alpha_1)^2}\frac{8\sigma'^3}{[f''(\alpha_1)(\alpha_2-\alpha)]^2}. \qquad \text{.....(7)}$$

I was led to this expression first through an oral remark of Dr C. Sykes. If one only wants to compare the rates of precipitation for various concentrations in the region of the B-rich mixed crystals, the above expression for A varies practically only through the first factor $(\alpha-\alpha_1)^{-2}$; the second factor is practically constant. Thus for the comparison in question of points near the boundaries of the phase diagram, the formula

$$A=\text{const.}/(\alpha-\alpha_1)^2 \qquad \text{.....(8)}$$

gives a quantitative measure of the difficulty of nuclear formation.

Naturally for a complete calculation of A one must make more detailed assumptions about the interatomic forces in the alloy. The simplest assumption is the one which Bragg and Williams introduced and of which Bethe, Peierls and others have made use, namely an interaction energy between neighbours only. With this assumption the calculation of the curve $f(\alpha)$ and the surface energy σ' between two phases of different composition presents no difficulty. In figure 4 we reproduce

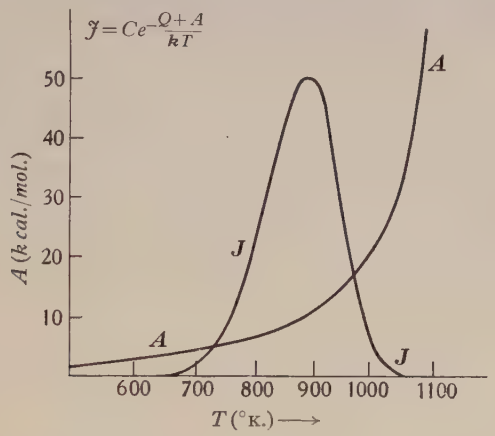

Figure 4. The energy A and frequency I of nuclear formation as functions of the temperature, according to (4), (6) and (8).

the results of the numerical calculation in one special case. These results are for an alloy with 15 atoms per cent of the component A, which is stable as a mixed crystal above 1211° K. and below this temperature separates as in figure 1. In figure 4 we show A as a function of the temperature, and also the frequency of nuclear formation

$$I = Ce^{-(Q+A)/kT},$$

with the value $Q = 39$ kcal./mol. The sharp maximum in I will be observed, which in this case lies 300° under the equilibrium line.

The assumptions made in this calculation of A could be improved in several respects. In the first place it is assumed in the calculation of A that the molecules A and B are distributed at random in a homogeneous phase, while in reality at any finite temperature the A atoms will always have more A neighbours than in the random distribution. Further, the composition of the nucleus in equilibrium is not given by α_2, since this value is only correct for a large precipitate of the phase; moreover, in the calculation of the surface energy σ' it is assumed that there is a sudden transition from the composition α_2 to α; probably one would obtain a smaller value of σ' through the assumption of a continuous transition. This correction should lead to a decrease in the energy A of nuclear formation, but the amount of this decrease cannot be predicted without detailed analysis.

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AGE-HARDENING OF COPPER-ALUMINIUM ALLOYS

By G. D. PRESTON, M.A., National Physical Laboratory

ABSTRACT. The ageing of aluminium alloys containing 4 per cent of copper is discussed. At room temperature the copper atoms segregate on the (100) planes of the crystal, but no new phase is formed. At 200° C. a pseudomorphic form of $CuAl_2$ is precipitated.

THE phenomenon of age-hardening presents a number of problems the solution of which would undoubtedly throw a considerable amount of light on more general questions relating to the strength of materials. Age-hardening occurs, or can be induced by suitable heat treatment, in supersaturated solid solutions; it is the outward and visible sign of a partially successful effort of the solution to attain a state of equilibrium characteristic of its temperature, by the rejection of the solute atoms as a separate phase. The application of X-ray methods to the examination of single crystals of an alloy of aluminium with 4 per cent by weight of copper has shown that it is possible to find out the way in which the copper is rejected from solution. Although this information does not enable us to form an estimate of the degree of strain present in the alloy, it does give a fairly detailed picture of how the copper atoms move during the course of the reaction.

The copper-aluminium alloy ages at room temperature after quenching from 500° C. This room-temperature ageing is accompanied by remarkable changes in the X-ray diffraction pattern of single crystals of the alloy. Certain well-marked streaks make their appearance on the photographs; at first these are faint and diffuse, but as ageing proceeds they become more intense and less diffuse. Their appearance after 3 days at room temperature is shown in figure 1. I have interpreted the streaks as indicating that the copper atoms are segregating on (100) planes of the crystal and that in these copper-rich regions the spacing of the crystal is a little less than that elsewhere; a local enrichment of the alloy with copper would be expected to produce a diminution of the spacing as the parameter of aluminium (4·041 A.) is reduced by copper in solution. At room temperature the reaction proceeds no further than the state which produces the streaks on the photographs; the hardness attains a nearly constant value after a few days and no noticeable change takes place in the X-ray diffraction patterns over a period of some months. Investigation of the high-order reflexions shows that at this stage there is no appreciable change in the value of the lattice parameter, which is generally assumed to indicate that no precipitation of a second phase has taken place; it is possible that only a small part of the available copper contributes to the formation of the plates of copper-rich material at room temperature.

An estimate of the size and distribution of the copper-rich patches can be made as follows. We suppose these regions to occur with regularity throughout the crystal on the faces of a cube of side Ma; this cube contains $4M^3$ atoms of which 1·75 per

cent are copper. If a fraction $1/p$ of the copper is associated with the copper-rich patches, then the number of copper atoms in these regions is $0{\cdot}07M^3/p$. We can take each patch to be a square of side Na and assume that copper atoms occur at the rate of one in every area a^2; if the patches are n planes in thickness, the number of copper atoms in each is nN^2 and there are three such patches associated with each cube of side Ma. Hence

$$M=(3pnN^2/0{\cdot}07)^{\frac{1}{3}}.$$

The X-ray evidence suggests that in the condition of maximum hardness at room temperature, $p=10$, $n=3$ and $N=10$, giving $M=50$. The copper-rich regions are thus scattered through the crystal at an average distance of about 200 A. from one another. The value of M is comparatively insensitive to changes in p and n, doubling either of these only increasing M by 25 per cent. The estimate here given of the size of the particles is rather smaller than that given by Swindells and Sykes [1] for

Figure 1. Laue photograph of aluminium-4 per cent copper single crystal aged 3 days at room temperature. X-rays parallel to [001]; [110] vertical. Distance from crystal to film 5 cm. A silver target operated at 60 kv. peak was used. In addition to the Laue spots there are "cross grating" spots due to the diffraction of Ag $K\alpha$ radiation by the sheets of copper. The plane (001), perpendicular to the X-ray beam, produces spots (11) on the longitudinal and vertical lines through the centre at a distance $r=1$ cm. from the centre; the points (20) lie at the extremities of the diagonal cross, $r=1{\cdot}4$ cm.; (31) and (22) can also be seen. The planes (100) and (010) produce spots at $r=2{\cdot}9$ cm. The intense central cross arises from these planes; it is largely due to the Ag $K\alpha$ radiation and the length of the arms is a measure of the linear dimension (about 40 A.) of the copper-rich plates. Reduced to $\frac{2}{3}$ of the original size.

the dimensions of the particles precipitated in the silver-7·5 per cent copper alloys during hardening.

The values of n and N used above have been confirmed by Guinier [2] as regards order of magnitude. As a result of his experiments he determines the thickness and linear dimensions of the copper-rich regions within rather closer limits than I have attempted. His conclusions are worth quoting as they so closely confirm my own. As regards the thickness of the regions, Guinier states that they are for the most part composed of one or two layers of atoms; this compares with my own estimate [3] of probably less than five and perhaps no more than two. After some days ageing

at 25° C., Guinier finds the linear dimensions of the patches to be about 45 A., increasing to 800 A. for the alloy aged at 150° C. for 16 days. These figures compare with my estimate of the dimensions of about 10 atomic distances (40 A.) after a few hours at room temperature, and about 10^3 atomic distances (4000 A.) after a few hours at 200° C. The agreement, especially at the lower temperatures, is sufficiently good to inspire one with some confidence in the accuracy of the picture we have drawn of the state of the alloy during the ageing process.

When the alloy fully aged at room temperature is subjected to heat treatment at 200° C., the first change is an immediate reduction in hardness. Five minutes' treatment at the elevated temperature reduces the hardness number to that of the alloy in the quenched condition. At the same time the streaks, which we have interpreted as being due to the formation of plate-like regions rich in copper, become much weaker on the X-ray photographs. It seems that the smaller copper-rich plates disappear, presumably much of the copper reverts to a random distribution, and the hardness falls. The absorption of heat, due to the "evaporation" of the copper from the regions of high concentration, or the destruction of a local ordered solid solution, has been observed by Swindells and Sykes [1], and their interpretation of this part of the $\{C_p, T\}$ curve is confirmed by the X-ray evidence.

If the heat treatment at 200° C. is continued, the hardness rises during the course of some 5 hours and ultimately exceeds that attained at room temperature. This increase of hardness is accompanied by a return of the streaks to the X-ray photographs, showing that plates are again being formed. The streaks when they reappear are always quite sharp, suggesting that the area of the plates is greater than that of those plates which are formed at room temperature. After the hardness has attained its maximum, further heat treatment makes the streaks break up into diffuse spots; the plates are thickening. The hardness falls as the treatment at 200° C. is continued and after 20 to 50 days the streaks have disappeared, the alloy is soft and there are well-developed diffraction spots on the X-ray diagrams which must be due to relatively large regions of a second phase, since they are quite well resolved. I have attempted to determine the structure of this phase and believe it to be of the CaF_2 type [3], so that its composition is $CuAl_2$. The crystals of this phase are nearly cubic (axial ratio 1·015) and the square faces fit into the aluminium lattice; there are three crystals of $CuAl_2$ in each aluminium crystal, one on each (100) face, a fact which complicates the analysis. This structure seems to be quite stable at 200° C., remaining unchanged after 50 days' treatment at that temperature. The change to the usual tetragonal form of $CuAl_2$ does not take place in single crystals until a temperature of 300 to 350° C. is used. At the latter temperature the reaction takes place quite quickly and the normal tetragonal phase is formed in an orderly manner from the existing crystals of the (nearly) cubic form.

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X-RAY EVIDENCE OF INTERMEDIATE STAGES DURING PRECIPITATION FROM SOLID SOLUTION

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ABSTRACT. Intermediate metastable structures resulting from the partial decomposition of solid solutions have been found in the Cu-Ni-Al, Fe-Ni-Al and Fe-Cu-Ni systems. In each case a single-phase structure, stable at high temperatures, breaks up into two phases on cooling. The first stage in the decomposition is the formation of islands, in which atoms are segregated prior to precipitation.

(1) Islands of $CuNi_2Al$ segregate from a copper-rich solid solution.

(2) Islands of FeNiAl segregate from an iron-rich solid solutions. These islands are recognized by the formation of the superlattices characteristic of the precipitating phases.

(3) During the decomposition of $FeCu_4Ni_3$ into two phases, a laminated structure is produced, in which copper-rich laminae alternate with laminae rich in iron and nickel. Each has a tetragonal structure with the same a axes as in the former solid solution; in the copper-rich laminae $c > a$; in the other laminae $c < a$.

During recent X-ray investigations of ternary alloy systems, new experimental evidence has been accumulated with regard to the initial stages of precipitation from solid solution. The primary object of the investigations was indeed to survey the phase diagrams under conditions which would give an approach to equilibrium at moderate temperatures. In practice, it was found difficult to get equilibrium anywhere near room temperature owing to the long periods required for heat-treatment. A rough idea of the time required to bring about phase changes by diffusion at different temperatures was obtained from some experiments on the iron-nickel system[1]. At 600° C., equilibrium conditions may be approached after about 1 day, while at 300° C. more than a year may be required. It is clear from the steepness of the time scale that in such alloys equilibrium conditions cannot be established below about 500° C. except by the prohibitive expenditure of time.

The object of the present account is to describe what happens to certain alloys when they are heated for shorter times than are necessary for the attainment of equilibrium. This is of very great practical importance, because it describes to some extent the condition which may be expected at room temperature, where true equilibrium can never be attained.

§ 1. THE COPPER-NICKEL-ALUMINIUM SYSTEM

A determination has been made recently of the copper-nickel-aluminium constitutional diagram[2]. Alloys in the $\alpha + \alpha_1$ two-phase region consist of mixtures of a copper-rich face-centred cubic phase together with a second phase, also face-

centred cubic but having a superlattice in which cube corners are distinguished from the centres of cube faces. In the ideal state, this superlattice is represented by the formula Ni_3Al, but it is capable of taking into solid solution large amounts of copper which replace nickel up to a limiting composition which is near $CuNi_2Al$.

The phase diagram indicates the directions of the tie-lines in the two-phase region $\alpha+\alpha_1$. Starting at first parallel to the nickel-aluminium side of the diagram, they gradually swing round until they finally follow the line $Cu-CuNi_2Al$. For example, an alloy with the approximate formula $Cu_{17}Ni_2Al$, which is a single phase at high temperatures, breaks up on cooling into a copper-rich phase and a phase with the approximate formula $CuNi_2Al$. If this process were completed, the following equation would represent the reaction

$$Cu_{17}Ni_2Al = 16Cu + CuNi_2Al.$$

In practice the equilibrium is frozen long before this stage is reached.

The precipitation of the superlattice phase begins just above 700° C. At 600° C. about half of the nickel and aluminium atoms have been thrown out of solid solution[3]. During experiments with alloys cooled at about 10° C. per hour it was shown that at this rate equilibrium could not be followed below 600° C. The amount of the precipitating phase could be deduced in two ways, either by a direct comparison of the strengths of the lines of the two phases or from an estimate of the strengths of the superlattice lines. The two methods give different results, much more of the precipitating phase being indicated by the superlattice lines than by the main lattice lines.

This result was explained by the formation of "islands" of α_1 within the α lattice. At first these form an integral part of the original lattice, so that the main lattice lines are not duplicated. The bulk of the solid solution is denuded of nickel and aluminium atoms which concentrate in the α_1 islands. The lattice spacing remains unchanged because the islands are not large enough to break away from the parent lattice. Later a certain proportion grow to the stage where they are able to break away and form separate crystallites with slightly different lattice spacings.

With the heat-treatment adopted, certain alloys (e.g. $Cu_{32}Ni_7Al$) had not broken up beyond the island stage; there was no sign of separate crystals of the second phase being present. This was probably because the alloy had only just begun to break up above 600° C. where diffusion is very slow. On the other hand $Cu_{17}Ni_2Al$ with this heat treatment showed some complete separation of the precipitating phase with additional material still in the island stage.

§ 2. THE IRON-NICKEL-ALUMINIUM SYSTEM

The iron-nickel-aluminium constitutional diagram[4], includes an area called $\beta+\beta_2$, where two body-centred cubic phases are in equilibrium. According to this diagram, for an alloy such as Fe_2NiAl, β is nearly pure iron, while β_2 approximates to the formula FeNiAl. Alloys near the centre of this phase-field show their two-phase character by the duplication of the most highly dispersed reflexions, especi-

ally from 220 and 310. The superlattice lines have a lattice spacing corresponding to the FeNiAl phase (2·878 A.) which is appreciably greater than the spacing of the iron-rich phase (2·868 A.).

In the alloys Fe_2NiAl and Fe_3NiAl the two phases appear to be present in about equal proportions. The intensity of the iron-rich constituent increases as the iron corner of the diagram is approached, while that of the superlattice phase increases as the nickel and aluminium contents increase. There is of course nothing abnormal in this behaviour, and it is natural to find that at a certain composition one or other of the phases disappears. For example, FeNiAl itself is not quite single phase, the powder photograph showing a trace of the lines due to the iron-rich phase.

At the other end of the two-phase region an alloy such as Fe_6NiAl, after slow cooling, is found to consist mainly of the iron-rich constituent, about one-seventh of the FeNiAl phase having been precipitated. This would suggest that the composition of the iron-rich phase is near Fe_8NiAl. In fact for alloys containing more iron than is given by this formula, there is no doubling of the 220 and 310 reflexions. The material therefore contains only one lattice. On the other hand, even with much more iron, there are present the lines of the β_2 superlattice, which are indicative of the presence of a second phase. This applies both to $Fe_{18}NiAl$ and $Fe_{16}NiAl$. Both these alloys are therefore in the island stage. Slow cooling has led to the separation of islands of FeNiAl which are still immersed in the parent lattice.

It is important to note that the development of such islands is mutual. If part of the lattice becomes richer in one constituent, the rest of the lattice simultaneously becomes richer in the other constituent. It is natural to regard the phase which is present in smaller amounts as the precipitating phase, but as we shall see in considering the FeCuNi alloys, this is a purely arbitrary distinction, since it is possible for the two segregating structures to be present in equal amounts.

It is interesting to speculate as to what would happen at lower temperatures if the alloys were less sluggish. Possibly the whole of the iron atoms would separate from the NiAl leaving two perfect types of structure without solid solution. The magnetic measurements of Snoek[5] made at room temperature suggest that this is the case, but the x-ray evidence does not support this conclusion. It is not impossible that a complete segregation may take place on a very small scale even with normal cooling rates.

§3. THE IRON-COPPER-NICKEL SYSTEM

Köster and Dannöhl[6] have shown that certain alloys which are single-phase face-centred cubic at high temperatures break up into two phases on cooling. In figure 1 the phase boundaries are shown for 1200°, 800°, 600° and room temperature respectively. An alloy such as FeCuNi is already two-phase at 800° C., whereas $FeCu_4Ni_3$ breaks up below this temperature.

Some recent x-ray results confirm the general trend of the boundary between 800 and 600° C. Two types of heat-treatment were given. In the one, alloys were quenched from 650° C. after heating for three days. In the other they were cooled at about 10° C. per hour from 800° C. to room temperature. For the present purpose

we are only concerned with the effects on certain alloys near the composition $FeCu_4Ni_3$, which become two-phase below 800° C.

The effect of quenching from 650° C. is to give a clear-cut two-phase structure for $FeCu_4Ni_3$ and neighbouring alloys. For example, this alloy and both $Fe_3Cu_8Ni_9$ and $Fe_3Cu_{25}Ni_{12}$ show two sets of x-ray reflexions, one corresponding to a larger and the other to a smaller spacing. The phase with the larger spacing is richer in copper; the other phase is richer in iron and nickel. To produce this effect a lengthy heat treatment is necessary. In these experiments the alloys were heated for a week at 650° C. Quite different results are given by short times of annealing as the following will show.

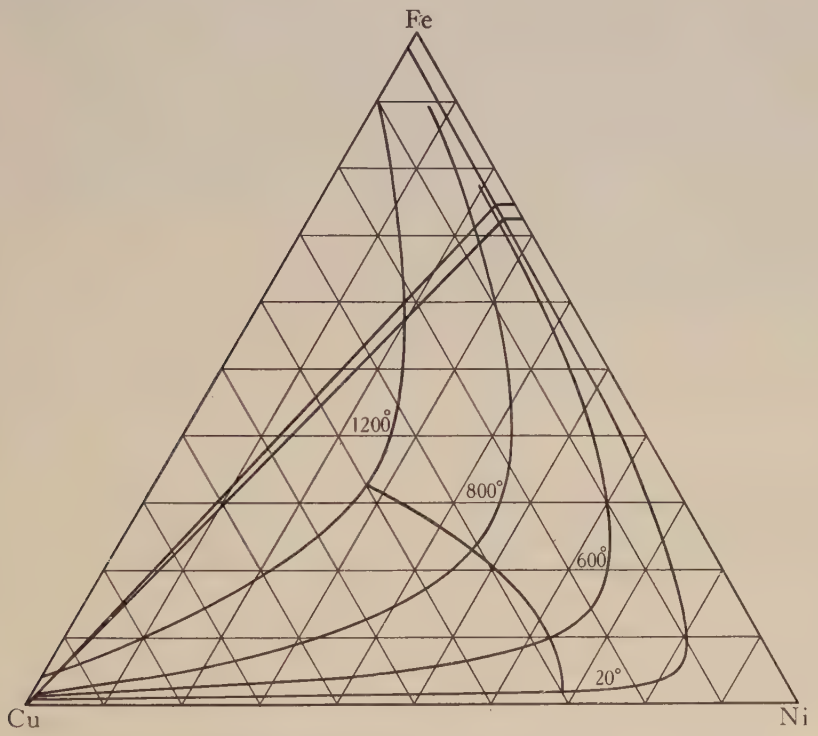

Figure 1. Iron-copper-nickel diagram according to Köster and Dannöhl.

The same specimens were allowed to cool from 800° C. to room temperature at about 10° C. per hour, but this was too rapid for the development of a clear-cut two-phase structure. On the other hand the structures obtained were certainly not single-phase. As in the case of the other ternary alloys which have been described, the two constituents have again been caught in the act of precipitating. The copper-rich phase and the phase richer in iron and nickel still form part of the same lattice, but the islands have already become partly independent of the parent structure. The nature of the islands will now be described.

Analysis of the powder photographs shows that certain of the face-centred cubic lines, as for example 222, are definitely resolved into two components, one of high

and the other of low spacing. In the absence of other data, this would suggest that the alloys had already broken up into two separate phases. On the contrary, the 400 line is not doubled. There is only one 400 reflexion visible on the powder photograph, though this shows definite resolution of the α_1 and α_2 radiations.

The most obvious interpretation of a powder photograph which shows a doubling of the 222 reflexion, but not of the 400 reflexion, would be that the structure was rhombohedral, but this is not the correct interpretation. The most conclusive evidence against this view is that there is no doubling of the 420 reflexion which must occur for a rhombohedral structure.

The only explanation which fits all the facts is that the original single-phase structure is breaking up into two phases, which are still only semi-independent of each other and of the parent lattice. In this intermediate metastable state, there is a close crystallographic relation of the phases to each other, and to both the original and final states of the alloy. At this stage, both phases are tetragonal, the axial ratios depending on the exact composition. $FeCu_4Ni_3$, which will ultimately break up into equal amounts of the two phases, already shows equal amounts of the two tetragonal structures. One of these has an axial ratio just greater, and the other just less, than unity.

The lattice dimensions are as follows:

α phase	$c = 3{\cdot}610$ A.	$c/a = 1{\cdot}009_5$
	$a = 3{\cdot}576$ A.	
α' phase	$c = 3{\cdot}549$ A.	$c/a = 0{\cdot}992$
	$a = 3{\cdot}576$ A.	

The important point to observe is that the two structures have identical a spacings; moreover this dimension is identical with the a spacing of the original structure.

The powder photographs yield a considerable amount of information concerning the way in which the two tetragonal lattices fit together. It was possible to draw the following conclusions:

(1) Islands of α alternate with islands of α' in each of the original crystallites.

(2) Neighbouring islands have their c axes pointing in the same direction.

(3) The islands are lamellae which have been formed on 001 planes of the original crystals.

(4) The average thickness of the lamellae may be about 100 A.

(5) The length and breadth of the lamellae may be about 1000–10,000 A.

(6) hko planes, which are perpendicular to the lamellae, are common to both types of structure.

(7) All other planes except hko are discontinuous at the boundaries of the lamellae.

Quantitative data are required to verify these conclusions, which are based on the following facts:

(1) hko reflexions are reasonably sharp (400 and 420 both give clearly resolved α-doublets on the powder photographs).

(2) 00l reflexions are considerably broadened. Only diffuse "tails" are visible to represent the 002 lines which should appear on either side of the 200 line; the 004 lines are so diffuse that they disappear into the general background.

(3) hkl reflexions are intermediate in sharpness. 202 and 313 are fairly sharp; 113 is blurred; 204 is lost in the general background.

Further work is required to trace the growth of the lamellae from their inception until their final disruption into separate phases. It may be necessary to examine single crystals, and to correlate the x-ray data with physical measurements.

The author is indebted to Prof. W. L. Bragg, F.R.S., for his interest in the research.

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AN ATTEMPT TO ESTIMATE THE DEGREE OF PRECIPITATION HARDENING, WITH A SIMPLE MODEL

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ABSTRACT. The process of diffusion being assumed to result simply in an interchange of atoms, an estimate is made of the internal strains produced by precipitation. According to the dislocation theory these strains are responsible for the hardness of the material, and so the degree of hardening can be predicted.

According to the dislocation theory of G. I. Taylor and Orowan[1], slip in a solid takes place through the motion of dislocations, which are generated in some way which remains obscure, but once generated will move under the influence of a small applied stress. According to Peierls[2] this stress must exceed a certain small value, which may however be neglected here. In cold-worked or age-hardened alloys the cause of hardness in crystals is the existence of internal strain. In figure 1, *ABCD* represents a solid possessing internal strains, so that a small block of the material *PQRS*, which would take the form of a cube if cut out of the block, has the distorted form of a parallelogram shown in the figure. Clearly,

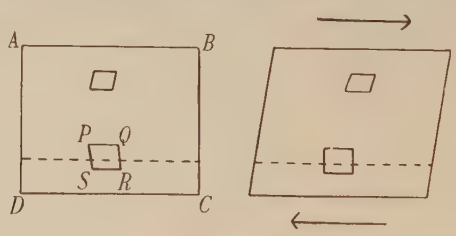


Figure 1.

if a stress is applied as shown by the arrows, no dislocation can travel along the dotted line until the strain is sufficient to bring *PQRS* back to the form of a cube. If the solid contains random internal strains, slip can only take place when the external strain is so great that the internal strain along the yield plane is everywhere in the same direction.

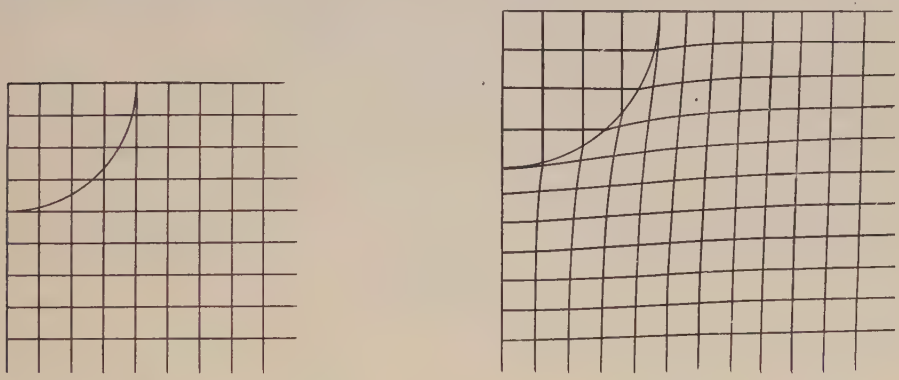
Let then S be the critical shear stress for the material, and let s (degrees) be the strain for this stress. Then the dislocation theory leads one to expect that s will be approximately equal to the *mean* internal strain in the material.

Our aim in this note is to calculate the hardness of an alloy in which a number of spherical precipitates have formed. Assuming that metallic diffusion consists

of a simple interchange of atoms, each nucleus will contain as many atoms of the precipitate as it originally contained of the original alloy. If the atomic volumes are different in the two cases, a state of strain will be set up.

Figure 2 shows the deformation of the crystal planes of an isotropic solid round a spherical occlusion. It will be seen that any piece of material in the matrix will suffer a shear strain; a piece which was originally a rectangle will now be a parallelepiped.

Consider then a spherical particle of radius r_0 embedded in the middle of an infinite matrix. As has been explained above, the number of atoms taken out from the hole is equal to the number put in; we shall assume that under zero pressure



(*a*) (*b*)

Figure 2. State of strain in a material due to an occlusion with a larger volume than the available hole (*a*) with the occlusion compressed to the atomic volume of the matrix, and (*b*) in equilibrium. The distortion illustrated here is that caused by an infinite cylindrical occlusion: this clearly illustrates the fact that the volume of a unit cell in the matrix remains constant during the expansion.

the atomic volume Ω_N of the material of the occlusion bears a ratio to that of the matrix Ω_M given by

$$\frac{\Omega_N}{\Omega_M}=\frac{(1+\delta)^3}{1}.$$

If δ is positive, the material of the occlusion will be under hydrostatic pressure; let its lattice parameter be reduced by a fraction $\delta-\epsilon$, where $\epsilon<\delta$, so that under pressure

$$\frac{\Omega_N}{\Omega_M}=\frac{(1+\epsilon)^3}{1}.$$

Let $x(r)$ represent the displacement of the medium at a distance r from the centre of occlusion. Elasticity theory gives as the most general form for $x(r)$ with spherical symmetry

$$x(r)=Ar+\frac{B}{r^2}.$$

In our case we may write

$$x(r)=\epsilon r \text{ when } r<r_0,$$

$$x(r)=\epsilon r_0^3/r^2 \text{ when } r>r_0.$$

Let the bulk modulus of the nucleus be K, and let the matrix have Young's modulus E and Poisson's ratio σ. The strain in the occlusion is a uniform hydrostatic compression $3(\delta-\epsilon)$, and hence the pressure p is given by

$$p=3K(\delta-\epsilon). \qquad \ldots\ldots(1)$$

In the matrix the radial and tangential strains are

$$-2\epsilon r_0^3/r^3 \quad \text{and} \quad +\epsilon r_0^3/r^3$$

respectively. Let the stresses be F_r, F_t, F_t. Then

$$\frac{-2\epsilon E r_0^3}{r^3}=F_r-2\sigma F_t$$

$$\frac{\epsilon E r_0^3}{r^3}=-\sigma F_r+(1-\sigma)F_t.$$

Equating p to F_r at the boundary

$$\epsilon=\frac{3K\delta}{3K+2E/(1+\sigma)}.$$

We may note that the strain in the matrix is a shear without dilatation. The shear at a distance R from the occlusion is

$$\epsilon r_0^3/R^3,$$

where ϵ depends on the materials only.

Consider now a single crystal containing N occlusions per unit volume, each of radius r_0. The average distance R of a point in the matrix from the nearest of them will be given by

$$R\simeq N^{-\frac{1}{3}}.$$

Thus the average shear strain s in the matrix is given by

$$s\simeq\epsilon r_0^3 N.$$

Thus if f is the ratio of the volume precipitated to the volume of the matrix, the average shear strain is

$$s=\epsilon f.$$

This gives, as we have seen, the shear strain at the yield point. The critical shear stress S is given by

$$S\simeq E\epsilon f.$$

We note that the critical shear stress is independent of the size of the occlusions and depends only on the quantity of metal deposited. This may not, however, be true for very small nuclei. We may expect that our strained regions must have a certain minimum size before they are effective in hardening the metal; a Taylor dislocation might jump a very small strained region.

The total strain energy is also independent of the size of the particles, for the energy associated with each sphere is proportional to

$$\int_{r_0}^{\infty}(\epsilon r_0^3/R^3)^2\,4\pi R^2\,dR=\tfrac{4}{3}\pi r_0^3\epsilon^2,$$

and this is directly proportional to the amount of matter in the particle of precipitate. We are attempting at the present time to apply these ideas to the non-spherical occlusions obtained in real cases, and a preliminary discussion is given in the next paper.

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THE INFLUENCE OF ELASTIC STRAIN ON THE SHAPE OF PARTICLES SEGREGATING IN AN ALLOY

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ABSTRACT. An estimate is given of the way in which the strain energy associated with a particle of precipitate depends upon the shape of the particle. It is shown that the energy can only be reduced if the precipitate forms in flat plates, and then only in the case of particles which have broken away from the lattice of the matrix. This dependence of strain energy on shape causes the precipitate to consist of plates of a shape similar to that observed in Widmanstätten structures.

When small quantities of a second phase precipitate out in an alloy, the internal strains set up affect both the hardness of the material and the nature of the precipitating particles. To fix ideas we may consider the precipitate to have the greater atomic volume. Without going further into the mechanism of diffusion, it is assumed that diffusion can only result in the interchange of pairs of atoms occupying definite lattice sites. In the process of segregation, particles of silver are formed which are larger than the vacant regions of the copper lattice which they occupy*. The elastic energies involved are large, and may exceed the chemical heat of solution of one phase in the other. Previous contributions to this discussion have shown that in the case of spherical particles the strain cannot be released by a simple agglomeration of the particles into larger spheres, and from general dimensional considerations it is clear that this result remains true whatever the type of strain, provided only that the distance between particles is large compared with their size, and that their size is large compared with a single atom. It will also be shown that even in the form of a sheet the silver atoms retain a large part of their elastic energy until the sheet breaks away.

What are the possible ways in which the strain energy can be released? The particle of precipitate is too big for the hole in which it is situated, and this misfit may be adjusted partly by compressing the silver and partly by increasing the size of the hole in the copper. The energy required to compress the silver until it fits the hole depends only on the size of the particle and not on its shape, so that changes in shape will not influence the accommodation of the precipitate. But, as W. L. Bragg has suggested, a disk-shaped hole in the copper can quite easily be expanded to accommodate the silver, for the faces of the disk will yield readily to internal pressure. The way in which the disk yields is shown by figure 1. What is now

* We use the Ag–Cu system as an example throughout.

needed is a calculation of the energy required to take a hole of volume of 1 cm.³ in a block of copper and increase its volume 1 per cent. This energy E depends upon the shape of the hole: the family of ellipsoids with semi-axes a, a, c represents disks, spheres or needles according to the value of c/a, and for this model the value of $E(c/a)$ is sketched as a function of c/a in figure 2. The details of the function are not yet known, but it is certain that the energy needed to enlarge the hole is greatest in the case of a sphere ($c=a$), and that it decreases to $\frac{3}{4}$ of this value as the sphere elongates to a needle ($c/a \to \infty$). For a very flat disk the energy tends to zero, and upper and lower limits for the slope of the tangent at the origin have been determined. An approximate value is taken in the following discussion.

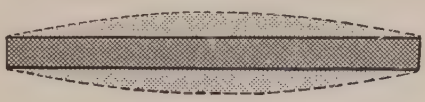

Figure 1. Under internal pressure the rectangular section of a flat disk becomes lenticular.

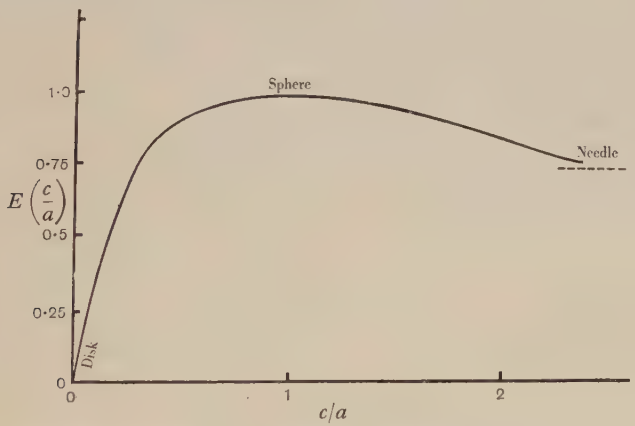

Figure 2. The elastic energy E of a particle of precipitate as a function of its shape. a is the equatorial diameter, c the polar diameter.

These considerations of elastic strain-energy seem to provide at least a qualitative explanation of the laminar precipitation which is observed in the Widmanstätten structures.

It is also possible to predict the influence of the degree of supersaturation of the silver on the shape of the particles which precipitate. The general nature of the effect is obvious. For suppose the alloy is so heavily supersaturated that every silver atom which diffuses to a nucleus sticks to it: then a nucleus originally long and thin gathers uniform coatings till its axes become nearly equal. On the other hand, in an alloy which is only slightly supersaturated, atoms can only precipitate on the edges of a disk-shaped nucleus, where they do not add much to the elastic energy. A layer of atoms precipitating on the face of the disk would cause an increase in the ratio c/a, and so an increase in the elastic energy of the particle which might be greater than the chemical free energy available.

If we insert approximate numerical values in the formula which is obtained, we find that for two phases whose atomic radii differ by 1 per cent and in which the precipitate is forming from an alloy 5 per cent supersaturated, the ratio of thickness to width should be about 1 to 25, which is very reasonable. But for Cu and Ag where the misfit is about 12 per cent a particle would apparently have to be 300 times as wide as it was thick before it could even begin to grow from an alloy 10 per cent supersaturated. It seems likely that the formation of nuclei of precipitation in such cases cannot be explained in terms of pure elasticity alone, but requires a special discussion of the matching of crystal planes in the two phases for each particular precipitation, such as has been carried out by Mehl and by Preston.

These considerations also supply a possible explanation of the {hardness, time} curves found in age-hardening. In the early stages the alloy is considerably supersaturated, and the particles of precipitate take the form of thick disks, growing rapidly. The strain energy and the hardness increase rapidly with time. But as time goes on the alloy becomes impoverished, and the rate of growth of the particles of precipitate diminishes. At the same time the thick particles tend to take up a more favourable thin sheet-like form, and so the strain energy and the hardness reach a maximum and diminish again.

Another possible cause of the softening, and the one which is probably effective in those cases where the Widmanstätten disks coagulate into globules on prolonged ageing, is recrystallization in the matrix. Returning again to spherical particles of silver, we note that the greatest strain in the copper matrix occurs just outside the particles of silver and that these regions will act as nuclei of recrystallization. Most of the energy of the copper is concentrated in a thin shell round the disturbing particle, so that most of the energy is released before the recrystallization has proceeded far. But the strain in the least strained regions of the copper, those farthest from particles of silver, is not released until practically the whole mass has recrystallized, so that the drop in hardness should occur some time after the crystal has given up its elastic energy. This effect may be the explanation of the secondary minimum of specific heat observed by Sykes in alloys near their maximum hardness.

As we have seen, a spherical precipitate will be compressed or expanded uniformly, while a thin sheet will have negligible strain energy. This will of course only be the case if the sheet has broken away; it is interesting to compare the strain energy of a sheet which has *not* broken away with that of a spherical precipitate.

Confining ourselves to crystals of cubic symmetry, we may take the tensor components of strain to be e_{ij}, when the energy in unit volume W is given by

$$\begin{aligned} 2W &= c_{ijkl}e_{ij}e_{kl} \\ &= c_{11}(e^2_{xx}+e^2_{yy}+e^2_{zz})+2c_{12}(e_{yy}e_{zz}+e_{zz}e_{xx}+e_{xx}e_{yy})+4c_{44}(e^2_{yz}+e^2_{zx}+e^2_{xy}). \end{aligned}$$

With these definitions the condition for isotropy is

$$2c_{44}=c_{11}-c_{12},$$

so that c_{11}, c_{12} and c_{44} agree with the constants tabulated by Schmid and Boas.

We define the components of stress F_{ij} by

$$F_{ij}=\partial W/\partial e_{ij},$$

and then

$$e_{xx}=\frac{(c_{11}+c_{12})\,F_{xx}-c_{12}F_{yy}-c_{12}F_{zz}}{(c_{11}+2c_{12})\,(c_{11}-c_{12})},$$

$$e_{yz}=F_{yz}/2c_{44}.$$

For uniform compression we may take $F_{ij}=F\delta_{ij}$, giving $e_{ij}=F\delta_{ij}/(c_{11}+2c_{12})$. If the linear dimensions of the particle of precipitate are altered in the ratio $1+\epsilon:1$, we must have $e_{ij}=\epsilon\delta_{ij}$ and $W=\frac{3}{2}(c_{11}+2c_{12})\,\epsilon^2$.

For a sheet lying along 100 and contracted in this plane the only components of stress which do not vanish are $F_{yy}=F_{zz}=F$, giving

$$e_{yy}=e_{zz}=\frac{c_{11}F}{(c_{11}+2c_{12})\,(c_{11}-c_{12})}.$$

Again putting $e_{yy}=\epsilon$ we find

$$W=\frac{(c_{11}+2c_{12})\,(c_{11}-c_{12})\,\epsilon^2}{c_{11}}.$$

The ratio of the work required for the sheet to that required for the sphere is

$$2\,(c_{11}-c_{12})/3c_{11}.$$

For silver we may take

$$c_{11}=12{\cdot}0\times10^{11},$$

$$c_{12}=8{\cdot}97\times10^{11},$$

and the ratio is approximately $\frac{1}{6}$. Taking ϵ equal to 12 per cent, the actual energy stored in a sheet of silver is 25 cal./g.

Before these results can be applied we must briefly consider the behaviour of the matrix. In the case of a spherical particle the pressure of the precipitate causes the matrix to expand, and so the energy of the whole system is reduced to something of the order of half the quantity calculated above. But if the particle takes the form of a sheet, it is clear that most of the accommodation is accounted for by a contraction of the sheet in its plane, for any stretching of the matrix parallel to this plane would involve an equally great strain spread over a much larger volume. Moreover we have assumed that the faces of the sheet are free to expand, but in fact unless the sheet is extremely broad and thin the necessary displacement of the matrix requires a further expenditure of energy which may not be negligible. So it seems that until the precipitate breaks away its elastic energy must always be quite large, of the order of the chemical energy released in the case of Ag-Cu.

DISCUSSION. PART II

Miss Marie L. V. Gayler, D.Sc. Mr Preston has shown by x-ray examination that, in the early stages of ageing, copper atoms segregate in the form of plates on (100) planes. Owing to the smallness of their dimensions it is not possible to detect such plates in a specimen under a microscope. I have, however, observed plates of the intermediate phase in a high-purity aluminium alloy containing 4 per cent of copper which has been aged for 27 days at 250° c. These plates must have as their origin the plates formed by the segregation of copper atoms in the early stages of ageing. The specimens examined are un-etched but have been swabbed with $\frac{1}{2}$-per-cent hydrofluoric acid during the polishing process. The intermediate phase can be detected by its very characteristic blue colour, in contrast with $CuAl_2$, which has a pale pinkish-yellow colour.

Figure 1 ($\times 2500$) shows plates of the intermediate phase scattered at random in the plane of polish, which must be parallel to (100) planes since in the matrix are thin plates of precipitate lying at right angles to each other.

Mr Preston has been unable to determine from x-ray examination whether the intermediate phase is a metastable intermediate phase or the stable form of $CuAl_2$ at room temperature. I have, however, been able to determine the nature of this transformation since I have observed the change taking place in all stages under the microscope.

In the grain at the left of the bottom of the photomicrograph, figure 2 ($\times 2500$), precipitation of the Widmanstätten type has taken place; while in the upper grain the precipitate has come out in thin plates which are at right angles to each other, showing that this surface must be parallel to (100) planes. Superimposed on it, and scattered at random, are irregularly shaped plates of the intermediate phase, blue in colour; but parts of some plates have changed into $CuAl_2$, since the colour of that portion is no longer blue but has the yellow colour of $CuAl_2$. Also, some smaller plates have changed completely into $CuAl_2$. In figure 2 the light particles are $CuAl_2$ and the darker toned plates are the intermediate phase. The high light on some of the plates indicates those portions which have changed to $CuAl_2$. It is extremely difficult to show this clearly in a photomicrograph, but the colour-difference is very definite under the microscope. Figure 3 ($\times 2500$) shows another grain with plates of the intermediate phase, some of which are changing to $CuAl_2$. These results are most important, for they show definitely that the transformation from the intermediate phase to $CuAl_2$ is polymorphic.

I have also obtained, from microscopic examination, evidence that more than one intermediate phase may be formed in ternary alloys. Figure 4 ($\times 2500$) is the photomicrograph of a high-purity alloy containing 4 per cent of copper and 0·5 per cent of magnesium, and aged 1 hour at 350° c. Besides the blue plates of the intermediate ($CuAl_2$) phase, buff-coloured plates are to be seen in the plane of polish when the latter is parallel to (100) planes. In figure 4 some of the thin needles (at right angles) are definitely blue, and are therefore of the intermediate

Figure 1. × 2500.

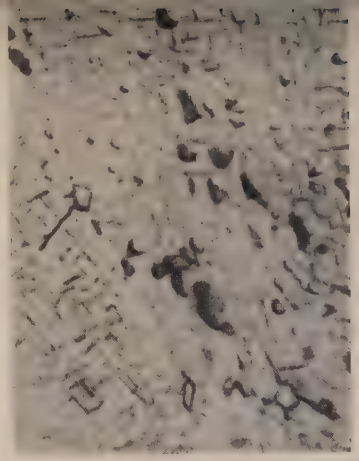
← Intermediate phase
CuAl2 →
← Intermediate phase changing to CuAl2
Intermediate phase → changing to CuAl2
← Intermediate phase changing to CuAl2
CuAl2 →

Figure 2. × 2500.

Figure 3. × 2500.

Figure 4. × 2500.

($CuAl_2$) phase, and on the right at the bottom of the photomicrograph is a triangular (dark) constituent which is the blue intermediate phase, on the left of which is a (light) piece of $CuAl_2$. The large plates are the buff phase, which appears to be changing into $CuAl_2$ as seen by the light edge on them.

An interesting fact, in confirmation of Mr Preston's statement that the new crystals (intermediate phase) are closely united to the aluminium lattice, is that the blue plates of the former have no definite outline but seem to merge into the aluminium matrix. When, however, the change to $CuAl_2$ takes place, a definite line of demarcation exists between $CuAl_2$ and the matrix on that side of the plate where the change has occurred.

Dr G. Wassermann. The explanation of the processes occurring during the age hardening of the aluminium-copper alloys has offered many difficulties, since it has been shown that there is no change of lattice constant and therefore no precipitation at room temperature.

This was the situation ten years ago, when Dr Hengstenberg and I measured the changes of intensity of the reflected x-rays during age hardening[1]. We found that the intensity changed as though the lattice were becoming poorer in its copper-content, and we concluded that the copper atoms were assembled at definite points in the aluminium lattice. At the same time similar suggestions were made by several authors, though from theoretical viewpoints. Further experimental progress seemed not to be possible with the experimental methods of to-day, and therefore Mr Preston is to be congratulated on his excellent results.

Mr Preston has reported further on the structure of the intermediate phase, which is precipitated at low ageing temperatures, for instance, 150° c. The lattice constants of the tetragonal cell, which he determined, are not the same as those found by Weerts and myself[2]. We found, as he did, that the tetragonal cell was situated with its *c* axis normal to the cube-plane of the aluminium. The difference is that, in our cell, *a* is in agreement as regards orientation and length with the side of the aluminium cube, whereas Preston chose the *a* axis in the direction [110]. I think that the differences are not great, and that the phase investigated in the two cases is the same. I am also glad to see that the times and temperatures found by Mr Preston for the forming of the intermediate phase and the $CuAl_2$ phase confirm my own results very well[3].

I should like to draw attention to still another point, which is perhaps of interest in a conference on internal strains; that is, the influence of quenching strains on age hardening. Phillips and Brick[4] were the first to point out this problem. If you quench specimens of different diameter of an age-hardenable aluminium alloy, you will find that the lattice constant increases with the diameter, as is shown for a technical alloy in figure 1[5]. The enormous differences in lattice constants are only to be explained by the presence of quenching strains. It is remarkable that the variations in lattice constants with diameter of the specimen are much smaller in unalloyed aluminium; therefore it is to be concluded that the supersaturation of the alloy increases the strains and also that the strains will

influence age hardening. This was shown also by another experiment[6]. Wires of different diameters of an aluminium-copper alloy were heated, quenched, and aged at room temperature in exactly the same manner. Figure 2 shows that there are differences in tensile strength which depend on the diameters of the wires. The tensile strength first increases and then decreases with increasing diameter. It was

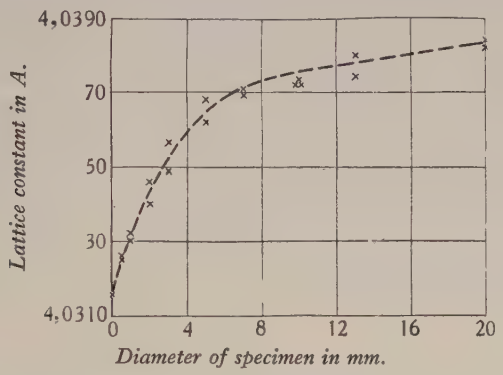

Figure 1. Lattice constants of quenched cylindrical specimens of a technical aluminium-copper-magnesium alloy.

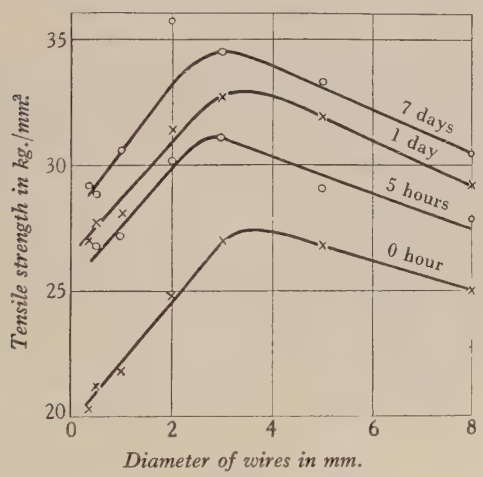

Figure 2. Tensile strength of aluminium-copper wires (4·8 % Cu) age-hardened at 20° C. for different times.

concluded that the tensile strength increases with the quenching strains, but that in the thicker specimens the tensile strength is lowered by the slower rate of cooling.

The influence of the quenching strains can also be seen by microscopic examination. Fink and Smith[6] have shown that in specimens of aluminium-copper alloys, age-hardened, for instance, at 150° C., there are to be seen precipitations in the form of striations. Our investigation[3] led to the conclusion that these

striations, figure 3, are mechanical twins, formed during quenching and caused by the quenching strains. If this conclusion was right, the twins must be present immediately after quenching, and the striations will only be spots of preferred

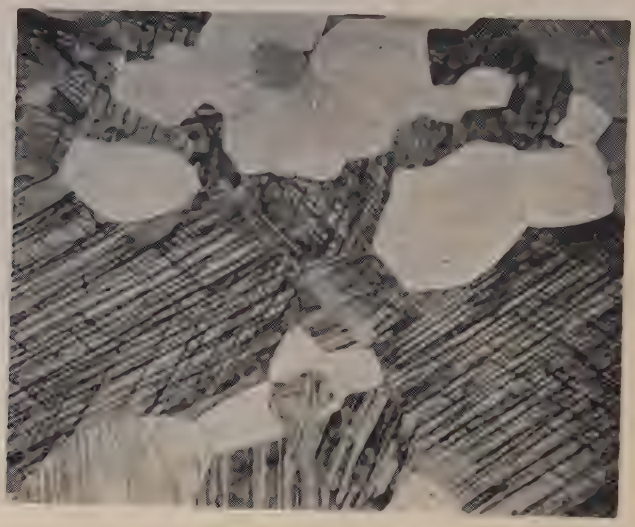

Figure 3. × 50.

Figure 4. × 1500.

Figures 3 and 4. Aluminium-copper alloy (4·8 % Cu) quenched from 530° C. and age-hardened at 150° C. for 20 days.

precipitation due to the deformation. Figure 5 shows that twins are in fact to be seen in the quenched specimen, and figure 6 shows that the striations of segregation are identical with the twins. The segregations do not fill the whole twin, but are in the form of single spots, as is to be seen in figure 4.

The effect of quenching strains is therefore also to be seen under the microscope. It seems that the influence of quenching strains is much greater in polycrystalline aggregates than in single crystals, where the cooling is more homogeneous.

Figure. 5. Aluminium-copper alloy, quenched from 530° C. in cold water, unetched. × 12.

Figure 6. Same specimen as in figure 5, aged 3 hours at 200° C., polished and etched. × 12.

In agreement with this conclusion, it was not possible to get quenching twins and precipitations therein in single-crystal specimens.

Not much is known to-day about the connexion between strains and age hardening, but I think that it will be worth while to give further attention to this point.

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Dr L. Frommer. In the course of an investigation into the effects of cold-working on aluminium alloys it was observed that the amount of cold-working effected, prior to solution treatment, influences the phase transition and the size of particle precipitated in artificial ageing[1]. Two specimens of Hiduminium RR. 56 alloy* were cold-rolled to reductions in thickness of 6 per cent and 86 per cent respectively, and were then solution-treated for one hour at 530° c., quenched, and aged for 16 hours at 170° c.

From both specimens x-ray patterns were taken (with Fe-K radiation by surface reflexion); these are shown together in the figure, the upper half of the picture representing the latter and the lower half the former specimen.

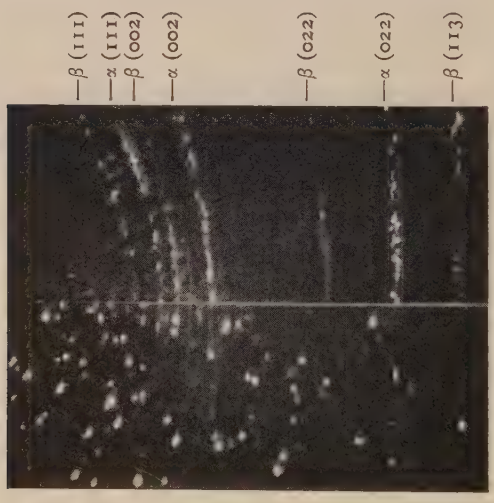
β (111)
α (111)
β (002)
α (002)
β (022)
α (022)
β (113)
Cold-rolled 86·5 %, solution-treated 1 hour at 530° c., quenched, aged 16 hours at 170° c.
Cold-rolled 6 %, solution-treated 1 hour at 530° c., quenched, aged 16 hours at 170° c.

Figure 1.

In both diffraction patterns the Debye-Scherrer lines $\begin{Bmatrix}220\\112\end{Bmatrix}$ and $\begin{Bmatrix}310\\202\end{Bmatrix}$ of the $CuAl_2$ crystals are clearly marked, but, besides these, the lower pattern shows a line (between $\begin{Bmatrix}220\\112\end{Bmatrix}$ of $CuAl_2$ and α (002) of aluminium) which is not present in the upper pattern, and the position of which agrees with that of the (224) reflexion

* The composition of the specimens was approximately: copper 2·4, nickel 1·4, iron 1·2, magnesium 0·8, silicon 0·8, titanium 0·07 per cent; the balance was aluminium.

of the intermediate phase described by Wassermann and Weerts[2]. Thus it appears that in the specimen that was cold-worked only lightly before solution-treatment, a considerable part of the intermediate phase is still retained after 16 hours' ageing at 170° C., whereas in the specimen that was highly cold-worked before solution treatment, the intermediate phase has been almost completely transformed into $CuAl_2$ during ageing.

Furthermore, photomicrographs which Dr Marie Gayler was kind enough to prepare from both specimens show the presence of precipitate in the grain boundaries of both, but the size of particles precipitated in a grain boundary of the specimen cold-rolled 86·5 per cent before solution treatment is appreciably greater than that of particles precipitated in a grain boundary of the specimen cold-rolled 6 per cent before solution treatment.

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Dr E. Orowan. Attention has been drawn to the elastic stresses set up by a growing nucleus in a solid matrix. These stresses can be taken into account by adding to the equation that gives the change of free energy due to the formation of the nucleus a term representing the elastic energy:

$$F = -F_m + F_s + F_e.$$

Here F_m is the absolute value of the difference between the free energy per unit of mass in the new phase and that in the old phase, multiplied by the mass of the nucleus; F_s is the surface energy, and F_e is the total elastic energy in the nucleus and in its surroundings. For a given shape of the nucleus, F_e is proportional to its volume; thus the elastic stresses have an effect as if the specific free energy of the new phase were increased by the elastic energy per unit of volume of the nucleus. In consequence, the temperature of the phase-transformation on cooling will be lower than the equilibrium temperature of the stressless phases, even if the cooling is extremely slow (unless the elastic stresses are released during the transformation by slip or otherwise). Similarly, the temperature of the transformation on heating will be higher than the equilibrium temperature of the stressless phases, even if the rate of heating is extremely small. Thus the transformation will show a hysteresis: the points A_r (temperature of thermal arrest on cooling) and A_c (temperature of thermal arrest on heating) cannot be brought to coincidence, however slow the heating and cooling. In fact it is well known that, in general, A_r and A_c do not coincide, except in cases like certain types of order-disorder transformations or the magnetic transformation at the Curie point. The difference between A_r and A_c cannot be attributed, as a rule, to difficulties of nucleus-formation caused by the comparatively high surface energy of small nuclei, since A_r and A_c represent fairly well defined limiting values towards which the observed temperatures of transformation converge for very slow rates of cooling and heating.

If the gap between A_r and A_c is due to elastic stresses, it should be possible to obtain from the knowledge of $A_c - A_r$, or of $A_c - A_e$ and $A_e - A_r$ (where A_e is the equilibrium temperature of the stressless phases), information about the magnitude of the stresses and thus about the mechanism of the formation of nuclei (the shape of the nuclei and so on).

The best known examples of extremely large transformation hysteresis are offered by iron-nickel alloys. Transformations of the martensitic type, furthermore, give examples of a hysteresis without appreciable time lag. The absence of time lag in the martensitic transformation of steel, for instance, is explained by the extremely small surface energy between nucleus and matrix; this is due to the fact that here nucleus and matrix fit together along almost identical lattice planes.

Dr W. G. Burgers. In connexion with Dr Bradley's paper I should like to mention an x-ray investigation of a single crystal of an alloy with the approximate composition Fe_2NiAl[1], which gave some information with regard to the structural changes that accompany the increase and decrease of magnetic hardness (coercive force) after heat treatment. The crystal, a rod measuring about $1 \times 1 \times 15$ mm., was cooled at different rates from 1200° to 700° C., the time of cooling, t, varying from a few seconds (quenching) to nearly an hour. The coercive force rose from $2\frac{1}{2}$ for the quenched state to 590 when t was about 45 sec., then decreased again to 260 for $t = 50$ min. The following features of the x-ray pattern seem of interest: with increasing coercive force the Co-Kα doublet lines, from the (310) reflexion, developed a more or less diffuse background of about twice the width of the doublet, the background, with increasing coercive force, gaining more and more in importance. The doublet lines, however, remained clearly visible and well separated. This was also true in the state with the highest coercive force.*

For longer times of cooling a general broadening sets in, while at the same time the coercive force decreases. Thus two states (lying at both sides of the maximum and obtained by applying different rates of cooling) with the same coercive force are characterized by totally different x-ray patterns.

The general broadening, which only becomes visible after the maximum in coercive force has been passed, was considered to be due to plastic flow of the stressed regions in the disturbed crystal lattice, as has been suggested by F. Preisach[2].

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Dr W. H. Taylor. Dr Bradley's results have some similarity to the preliminary results which have been obtained in the investigation of segregation in mixed potash-soda felspars. In pure potash felspar the alumino-silicate framework is held wide open by the large potassium ions, while in pure soda felspar the

* This feature is unfortunately not clearly discernible in the photograph 3*e* in the above-mentioned paper.

framework is partially collapsed because the sodium ions are small. The potash-soda felspars are observed both as homogeneous crystals, in which on the average the potassium ions and sodium ions are uniformly distributed throughout the framework, and also as lamellar crystals in which potassium-rich and sodium-rich sheets alternate and produce the various perthitic structures.

In any perthitic felspar the crystallographic axes a, b, c of the potassium-rich lamellae are roughly parallel to the axes a', b', c' of the sodium-rich lamellae, but in the orthoclase microperthites which we have examined there are significant differences in detail which appear to depend in the first place upon the proportion of soda felspar in the specimen. With less than about 30 per cent of soda felspar the relative orientation of the lamellae is of one type, with more than 30 per cent it is usually of a different type: a difference in thermal history of the specimen may, however, bring a soda-rich specimen into the structure type corresponding to a low soda-content.

Experimental data are more easily obtained for felspars than for the metals which have been described, but the interpretation is much more complicated on account of the low crystallographic symmetry; nevertheless, it seems clear that the segregation effects are similar in the two cases, and that the theoretical discussion of one problem may have immediate application to the other.

Prof. N. F. Mott. As the preceding papers have shown, one ought to make a distinction between nuclei or precipitates which have broken away from the parent lattice and those which have not; the latter include Preston's sheets, and the islands mentioned by Bradley. They are often referred to as "knots".

If the atomic volume of the precipitate is greater or less than that of the matrix, its presence in the matrix will lead to a certain amount of strain energy. This energy will affect the shape of the precipitate. If the precipitate has broken away from the matrix, the strain energy will be a maximum for a spherical occlusion, and zero for a thin plate. It has been suggested by W. L. Bragg that this strain energy is the origin of the Widmanstätten patterns observed in many alloys, and also the cause of the phenomena in felspars reported by W. H. Taylor in this volume. The paper by Nabarro attempts to calculate the shape to be expected.

If the nucleus does not break away, the strain energy will still be a minimum for a plate-like structure, but will be by no means zero; the precipitate can take up its proper specific volume, but it will be under shear.

Rough calculations (Nabarro) suggest that for the case of silver in copper the strain energy is so large as to prevent the formation of a stable nucleus at all; the precipitation of a silver-rich alloy in the matrix of copper would always lead to an *increase* in the free energy. Thus no stable nucleus is possible until the nucleus has become big enough to break away from the parent lattice. This would make it even more difficult to form a nucleus than was anticipated by Becker.

I should like very tentatively to suggest that the sheets found by Preston in Al-Cu alloys are formed in circumstances such as this. I suggest that no stable nucleus, measuring several atomic distances each way, can be formed in the parent

lattice, but that, for some reason at present not understood, the formation of sheets one atom or a pair of atoms thick does lead to a decrease in the free energy. The copper in solution will thus be in equilibrium with the copper in the sheets.

The sheets will act as nuclei on which the precipitates shown by Dr Gayler are built up, and these have of course broken away. The orientation of the sheet determines the orientation of the plate-like crystal which is built up on it. On the other hand, the fact that the crystal grows in a plate-like form at all is, in my opinion, due to the strain energy as explained above.

That sheets are formed in copper-silver alloys is supported by some results of Mehl[1], who finds that, with slow cooling, copper-rich precipitates are formed in a silver-rich alloy in plates parallel to the (100) plane, while silver-rich precipitates are formed in a copper-rich alloy in sheets parallel to the (111) plane. This strongly suggests that the precipitates have been formed on nuclei which are sheets one atom thick; one would expect the small copper atoms to segregate on (111) planes, where they are as close together as possible, while the large silver atoms would go into the (100) plane.

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III. POLYCRYSTALLINE METALS AND THE EFFECT OF COLD WORK

THE STRUCTURE OF A COLD-WORKED METAL

By W. L. BRAGG, F.R.S., Cavendish Laboratory, Cambridge

ABSTRACT. It is suggested that a cold-worked metal is in dynamical rather than statical equilibrium. An analogy with the state of affairs in superlattices is made.

§ 1. MOBILITY OF ATOMS IN A METAL

In contrasting the physical properties of a pure metal in the state of a perfect crystal, and those of a mass of differently orientated crystallites such as are produced by the distortion due to cold-working, one of the significant features is the stability of the cold-worked state. When once destroyed, the perfect crystalline arrangement is not restored by a rearrangement of the atoms. On the other hand, there appears to be an approximate lower limit to the size of crystallites produced by distortion however severe and long continued, the average dimensions being of the order of 10^{-4} cm., though this of course may vary with the metal and the temperature. Taylor and his collaborators have shown that the energy bound up with the lattice distortion and intercrystalline boundaries is of the order of 0·2 to 0·5 cal. per gram, and this energy would be released if the metal self-annealed to large perfect crystals. The obstacle to this process cannot be a restriction of movement of the atoms over each other. Interdiffusion takes place at relatively low temperatures, being quite rapid for instance in the case of copper and gold at a temperature of 250° C. Diffusion implies the drift of atoms over a very large number of interatomic distances in the lattice, and if this is possible the slight readjustments of relative atomic position required to transform an amorphous arrangement of metal atoms into a regular arrangement or for one crystal to grow at the expense of another are trivial in comparison. Changes in the degree of superlattice order in Cu_3Au, as Sykes has shown, take place at even lower temperatures than those at which diffusion is appreciable, as is to be expected because such changes only involve transposition of neighbouring atoms. It is difficult to see how an amorphous state can exist over any appreciable volume in a pure metal. When two crystallites of different orientations meet, there may be a transition layer two or three atomic diameters in thickness where the arrangement is irregular, but this can only extend to atoms which are simultaneously under the influence of both types of crystalline arrangement. A macroscopic "Beilby layer" between the crystallites is very difficult to conceive, for the atoms in the centre of it, being quite free to move, would immediately take up a regular crystalline form. An amorphous solid such as

vitreous silica can be frozen into a state of almost indefinite permanence because the bonds between neighbouring atoms are so strong. Once formed in an irregular way as the liquid cools, they become permanent at lower temperatures since the chance of a thermal fluctuation being sufficiently powerful to break all the bonds and permit rearrangement in any localized area is vanishingly small. On the other hand, in a metal kT is sufficiently great to permit rapid rearrangement right down to room temperature. Certain crystalline changes in iron-nickel alloys* can be brought about by plunging them into liquid air, which shows that even at $-180°$ C. changes in atomic positions take place freely. We cannot, therefore, suppose that the permanence of the cold-worked state is due to the freezing in of the thin transition layers between one crystal and another. These layers are free to move by the atoms in them changing their allegiance from the crystalline scheme on one side to that on the other, and the persistence of the mass of differently oriented crystallites, or their reluctance to self-anneal into large regions of perfect crystal, must be due to the assumption of certain forms of dynamic stability by the boundaries. Thermal fluctuations cause them to move about over small ranges in the crystal, but they tend to return to their mean positions.

§ 2. FOAM STRUCTURE IN ALLOYS WITH A SUPERLATTICE

In this brief note I wish to discuss an analogy which may be drawn between the state of a cold-worked metal and that of the "nuclei" of superlattice order in the alloy Cu_3Au which has been so fully studied by Sykes[1]. The superlattice order in Cu_3Au, as was first shown by Borelius, Johansson and Linde, is one in which gold atoms are at the corners and copper atoms at the face centres of a face-centred cubic lattice. The face-centred lattice is composed of four equivalent simple cubic lattices, any one of which may be chosen for the sites of the gold atoms. At temperatures above 381° C., copper and gold atoms are distributed on all four lattices in a way which is random except for the short-distance order of Bethe. Below this temperature order rapidly sets in.

The nuclei studied by Sykes can be likened to the domains in a ferromagnetic. Order may set in within a single crystal according to four different schemes. It starts from many centres in the cooling crystal and grows outwards, and when two different schemes of order meet there will be a transitional region where atoms have a divided loyalty. Sykes has studied these nuclei by measurements of energy content, electrical resistance, lattice spacing, and breadth of superlattice lines in x-ray powder photographs. He has shown that the average extent of the nuclei or domains depends on the thermal treatment. He has been able to produce a range of sizes varying from a diameter of about 40 A. to domains so large that the properties merge into those to be expected for a consistent scheme throughout the whole crystal. The smaller nuclei are produced by rapid cooling through the critical temperature, and the extended order by annealing it for 50 hr. a few degrees

* I.e. the change from face-centred cubic to body-centred cubic structure in the iron-rich alloys.

below the critical temperature. The various methods give consistent measurements of average size in any given case.

Two interesting points emerge from Sykes' work. The first is the surprising stability of a given coarseness of grain of the nuclei or domains. Resistance-temperature curves show that the order-disorder change proceeds reversibly inside each domain with its consequent characteristic effect on resistance, but that the additional resistance due to the boundaries remains constant. The observations which led Sykes to this conclusion are too extended to repeat here, but the point is proved in a convincing way. The second point is the narrowness of the transition layer. Its thickness is estimated by measuring the size of the nuclei by x-ray diffraction methods, and simultaneously measuring energy content, electrical resistance, and lattice spacing. The conclusion is reached that the transition layer is only two or three atomic diameters in thickness.

The stability of the domain structure may be explained by comparing these transition layers to the films which separate bubbles in a foam. As explained above, a transition layer can move freely by atoms transferring their allegiance from the order scheme prevailing on one side to that prevailing on the other. The fact that the order-disorder change takes place inside each domain shows that there is no obstacle to such a movement. If a promontory of one type of order (A) extends into a region of another type (B), it will shorten because the atoms at the tip have more neighbours conforming to the B scheme than to the A scheme. It will shrink until the boundary is flat or has equal opposite curvatures in two directions at right angles. It behaves, in fact, like a film with surface tension, the additional energy being due to the atoms in the boundary layer necessarily having some "wrong" neighbours. The existence of four types of superlattice A, B, C, D is essential to stability. Three neighbouring domains ABC meet along a line, and this line moves about in the crystal until the angles between the transition layers are so adjusted that no one domain tends to grow at the expense of the other two. Four domains $ABCD$ meet at a point with a similar adjustment of angles. The analogy with a foam is not complete, because the surface tension may vary with the relative orientation of the crystals and boundaries, but the principle is the same.

Picturing the formation of the nuclei, we must suppose that the different schemes start at random centres and grow. When they meet, they adjust their boundaries like the bubbles of a newly formed froth. Many of the domains disappear in this process. For instance, if an A scheme happens to be surrounded by B schemes, it will be eaten up by these neighbours. Finally, the whole settles down to equilibrium, and once this is established it is of a very persistent type. Small thermal fluctuations in boundary involve increases in energy, and so their range is restricted.

This view of the foam structure is borne out by a contrast of CuZn and Cu_3Au. CuZn has a body-centred cubic structure. Below 469° C. superlattice order sets in, the atoms of one kind being at cube corners and those of the other kind at cube centres. There is no evidence, however, of the formation of nuclei or domains. We would not expect their existence to be possible, because there are only two types of superlattice. A boundary between the two types may be stable, but there cannot

be three types meeting along a line or four at a point. The only possible domain structure would therefore be a set of laminae, and it is highly improbable that such should be formed by growth from random nuclei. Hence we conclude that a type A grows at the expense of B, or vice versa, over large volumes in the crystal, and this is borne out by measurements of electrical resistivity and energy content. These properties when plotted against temperature follow reversibly the same curves for all rates of heating and cooling.

§ 3. FOAM STRUCTURE IN COLD-WORKED METALS

Arguing by analogy, may not the same state of affairs exist in a cold-worked metal? It is of course no new idea to compare the boundaries between the crystals of a metal as revealed by etching to the structure of a foam[2]. What is referred to here is not the boundaries between crystals grown from the melt, but those between the crystallites produced by cold-working and distortion which are much smaller (10^{-4} cm.) and may only differ slightly in orientation. The conceptions which may be carried over are: (*a*) the boundaries between differently oriented crystallites are only a few atoms in thickness, and (*b*) the boundaries are not "frozen" in position but are in dynamic equilibrium.

The first effect of distortion of a perfect crystal is to produce these domains on a coarse scale, and the scale becomes smaller as distortion proceeds. There will be, however, a fairly definite limit to the fineness of grain. A very small domain is certain to be swallowed up by its neighbours. Consider, for instance, the rather artificial case of a thin layer of orientation A between two crystallites of orientation B. This is temporarily stable, but thermal fluctuations cause its boundaries to wave about. If at any point the film becomes momentarily so thin that the atoms at that part have more effective neighbours with the B scheme than with the A scheme, the film will burst and disappear by B eating up A. A very general line of argument shows that the probability of this happening in a given time, say 1 sec., varies in a characteristic way with the thickness of the film. If the probability is of the order unity for a thickness t, it will be extremely small ($\sim 10^{-13}$) for a thickness $2t$ and conversely extremely large for a thickness $\frac{1}{2}t$. If, therefore, the metal is thrown into an amorphous state by the distortion, it will rapidly self-anneal up to a certain coarseness of crystallite size, but beyond that point the process will become so slow that the metal remains in an approximately constant condition though not in true equilibrium.

Pictures of the mechanical strength of crystals, contrasting the ease of slip in the perfect crystal with the rigidity of the cold-worked crystal, are based on certain conceptions of the nature of the faults or departures from perfection in the crystalline structure. Such faults might be places where atoms are absent, or where one sheet of atoms lies incompatibly over another, such that n rows in one sheet are opposite $(n+1)$ rows of the other. The present picture does not differ essentially from others, except in that it is suggested that the faults readjust themselves in the distorted crystal until they become thin surfaces of transition between regions which

are perfectly crystallized right up to the boundaries. Some such structure is indicated by the necessity of reconciling the permanence of the cold-worked condition with the freedom of the atoms to readjust their relative positions. One other feature of such a picture may be pointed out. If the metal contains foreign atoms, such atoms will concentrate on the interfaces between the crystallites. A foreign atom in the otherwise perfect lattice must involve an increase in energy, whereas in the interface where the arrangement is irregular there are certain to be suitable positions where the replacement of an atom *A* by a foreign atom *B* will lead to a decrease in energy. Boundaries which are defined by the presence of the foreign atoms cannot move with the same freedom as those which are merely transitions from one crystallite to another, because if they move, there must not only be rearrangement but also movements of the atoms in following up the boundaries. This suggests an explanation of the marked effect of very small additions of foreign atoms both on the mechanical properties and on the rate of self-annealing of an alloy.

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CRYSTALLINE STRUCTURE AND DEFORMATION OF METALS

By W. A. WOOD, National Physical Laboratory

ABSTRACT. A survey is made of changes in crystalline structure of polycrystalline metals and large single crystals subjected to deformation by cold-work and by static and cyclic stressing, observations being made by a combination of mechanical, metallographic and x-ray tests. It is shown that the grains may be dispersed into crystallites characterized by a lower limiting size depending on the metal and that it is possible to observe internal lattice strains which it is considered are related to the process of strain hardening. It is also shown that the response of the crystalline structure depends on the manner and particularly the speed of application of stress, and that it is possible in this way to inhibit the dispersed crystallite formation and suppress the primitive yield-point of a metal, thus varying the hardness independently of the external deformation.

The deformation of a ductile metal raises the problems of the process by which the grains take up change in shape, and also of the hardening and modifications in other physical properties brought about by the progressive strain. The first occurs mainly by the action of slip, the chief features of which have been elucidated by the early work of Ewing and Rosenhain, followed by that of Taylor and Elam, Mark and Polanyi, Gough, Andrade, Orowan and others. The second process is still incompletely understood, and, on the experimental side, considerable data has been published which it is difficult to correlate satisfactorily. Latterly, information on both aspects has been extended in certain directions by the application of x-ray diffraction; it is proposed to outline some of these results, which have been obtained in conjunction with mechanical and metallographic tests, a combination which does at least serve to emphasize the more important factors involved.

§ 1. LOWER LIMITING SIZE OF CRYSTALLITES

Much of the work has been made possible by commencing with annealed material initially free from the effects of cold-work, and it will be convenient to refer to figure 1, which is a normal x-ray photograph of such a standard condition. The photograph shows the diffraction rings to consist of sharp isolated spots, each of which is a reflection from a highly perfect grain as defined by the grain boundary of the usual photomicrograph. The first obvious effect of plastic deformation, illustrated by figure 2, is to cause the spots to spread out into long arcs along the diffraction ring in a manner which indicates that the grains are dispersed into independently reflecting units. These will be termed crystallites to distinguish them from the metallographic grain. On continued deformation the arcs extend and the rings become continuous; the effect is the same whether one starts with

polycrystalline metal or large single crystals and shows that the crystallites are formed within each grain with crystallographic orientations differing extremely from the orientation of the parent grain; at the same time the microscope may show only small changes in shape of the grain boundary.

It is possible to set an upper limit to the size of the crystallites from a knowledge of the number of reflection spots which would be required to coalesce into a continuous arc or ring, and by calibration experiments with known grain sizes. In this way it can be shown that with the usual experimental dispositions the *continuity* observed means that the crystallites must be less than some 10^{-4} cm. It is next possible to set a lower limit to the crystallite size from consideration of the Scherrer effect, by which the resolution or radial width of the continuous arc depends on the particle size. In practice this effect does not become appreciable until the particle size becomes less than about 10^{-4} cm.; thus, in some typical experiments on aluminium, with a particle size of 10^{-4} cm., the line-breadth as measured on the photographic film for a line highly sensitive to the effect would increase by the barely noticeable amount of $\frac{1}{10}$ mm.; but with a size of 10^{-5} and 10^{-6} cm., the same line would broaden by respectively 1 and 10 mm. These figures are quoted to show that the line-breadth affords a sensitive indication of any reduction in size of the crystallites below the upper limit of 10^{-4} cm. fixed by quite different considerations. Now it is found that in progressive deformation carried on to the severest extent practicable, the line-breadth quickly reaches a maximum which is then never exceeded and which has a characteristic value for a given metal at a particular temperature of deformation. In part this broadening may be due to lattice distortion, but, as a result of work on the whole sequence of changes, the writer has pointed out that, whatever the cause, the existence of the maximum value automatically sets a lower limit to the size of the crystallites into which the grains can be broken down by deformation, and further, that the striking contrast between the ease with which the initial breakdown is produced, on the least permanent deformation, and the subsequent impossibility of reducing the crystallites below this limiting size, shows that the crystallite must be regarded as a fundamental unit of the metallic grain. The lower limits calculated from the Scherrer formula, and the measured line-breadths, for some typical pure metals are as follows: Cu, $0{\cdot}7 \times 10^{-5}$ cm.; Ag, $0{\cdot}8 \times 10^{-5}$ cm.; Ni, $1{\cdot}2 \times 10^{-5}$ cm.; Al, 10^{-4} cm. (no appreciable line-broadening); Fe, $3{\cdot}2 \times 10^{-5}$ cm.; Mo, $2{\cdot}2 \times 10^{-5}$ cm. It will be seen that the crystallites are very far from being amorphous.

So far as experiments have gone, the only way of lowering the limiting size at room temperature is by the addition of certain forms of impurity to the metal. A change of this type is shown by figures 5 and 6, the former showing the maximum line-broadening obtainable for pure iron and the latter for a 0·1 per cent carbon steel. Similar changes are brought about by the co-deposition of oxide, hydroxide or gases in electroplated metals, or by the "addition agents" purposely added, as in the recently developed bright nickel plating.

The instability of a crystallite size less than the above lower limit explains the observation by a number of workers that the ultimate periodicity of the pseudo-

regular slip lines which appear in the deformed grains is of the same order of magnitude, 10^{-4} to 10^{-5} cm. It is difficult, however, to reconcile this instability, further confirmed by the next section, with the amorphous Beilby layer shown by electron diffraction to exist on the surface of a mechanically polished metal, unless it is assumed that this film is not typical of the pure metal, normal crystallite growth being inhibited by the finely divided impurities introduced by the polishing media.

§ 2. PERMANENT LATTICE STRAINS

The point arises as to how much of the overall deformation of a metal can be transmitted to and permanently held by the atomic lattice. This aspect is of particular importance, because, as shown later, the external strain exhibited by a metal bears no direct relation to the degree of strain-hardening but depends in an arbitrary fashion on the mode of application of the deforming stress. The internal lattice strain or lattice distortion is the active factor in this connexion, as also in magnetic hardness.

Such strains have been observed and measured in some recent work, which may perhaps be conveniently illustrated by the reproduction of some photographs of cold-rolled pure copper of which figure 1 represents the initial state and figure 2 the state after 4 per cent reduction in thickness. It was found that on further deformation the diffraction line first broadened to a definite maximum and then contracted to an equally characteristic minimum value, the processes alternating as the deformation proceeded. At the same time, the size of the unit cell increased as the line became abnormally diffuse and decreased when the line-breadth diminished; moreover, the expanded value was greater than, and the contracted value less than, the standard lattice dimensions as given by the initial annealed material. The expansion effect is illustrated by figure 3 taken after 80 per cent reduction, and the recovery effect by figure 4 taken after the reduction had been continued to 85 per cent. In these photographs the inner ring is the (400) $\alpha_1\alpha_2$ doublet and the outer ring is the (331) β; the difference in the reflection angles is enough to render the former much more sensitive to lattice changes so that, when such changes occur, the distance between the rings should decrease. A comparison of figure 3 with either figure 2 or figure 4 shows this relative shift quite clearly, despite the increase in diffusion of the (400) ring in figure 3 where the expansion has taken place. It is particularly interesting to note that the distortion thus exhibited by the lattice is shown to be of the nature of a volume expansion, for the (400) ring is made up of reflections from the mutually perpendicular (400), (040) and (004) planes, and all these spacings must have increased. The abnormal diffusion accompanying the expansion effect is attributed to irregularity in such expansion and not to further breakdown of the crystallites, for similar variations in lattice spacings were found in metals such as pure iron, where the maximum line-broadening is very small, without noticeable changes in line-breadth. The residual broadening in the recovered state is explained by the Scherrer effect and gives the minimum crystallite size. The difference between the lattice spacing of the recovered

Figure 1. Cu, initial.

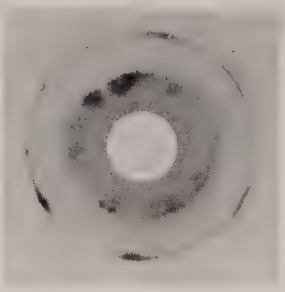

Figure 2. Cu, 4 per cent reduction.

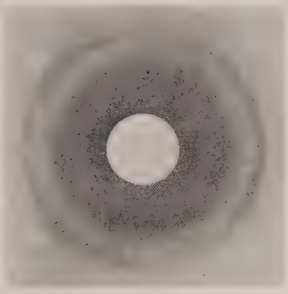

Figure 3. Cu, 80 per cent reduction.

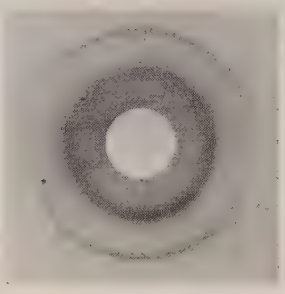

Figure 4. Cu, 85 per cent reduction.

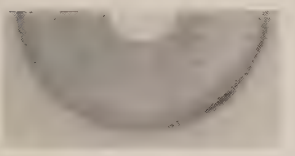

Figure 5. Fe, purity 99·96 per cent (maximum line-broadening).

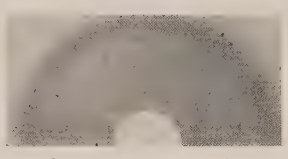

Figure 6. 0·1 per cent carbon steel (maximum line-broadening).

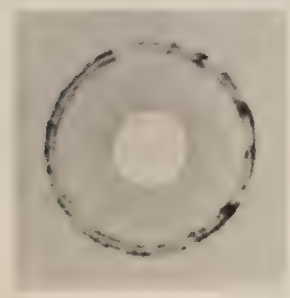

Figure 7. α brass (after static load 9 ton/in^2).

Figure 8. α brass (after 3×10^4 cycles at ± 9 ton/in^2).

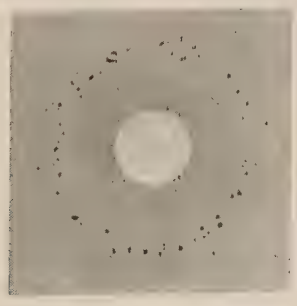

Figure 9. α brass (initial state).

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state and the standard spacing of the initial large annealed grains is taken to indicate the influence of the surface atomic layers which in the small crystallites form an appreciable proportion of the whole volume; this influence appears to assume a form analogous to a surface tension and is observable as soon as the grains break down.

The observed recovery effect is not to be confused with recrystallization, which of course would give an x-ray photograph similar to the annealed condition. In pure silver it was found that after severe deformation the recovery process became more violent and recrystallization proper did then occur after an interval of time which became shorter as the deformation proceeded. The term recovery is thus used in a particular sense, being concerned only with the removal of a superimposed distortion from the lattice of the various grains and thereby distinguished from recrystallization which results in the formation of entirely fresh grains. These observations explain the well-known phenomenon that it is possible largely to recover the initial softness and other mechanical properties of a metal by heat treatment at temperatures well below those required to renew the properties by recrystallization.

Some importance is attached to the actual observations of an expansion and a recovery effect because they demonstrate, first, the nature and extent of a distortion which the atomic lattice of a deformed metal can take up and retain, and, second, that the distorted state is not one of stable equilibrium (since it can be upset by continued deformation). Typical measurements on a group of pure metals are as follows, the contraction being reckoned from the standard spacing of the unit cell but the expansion from the contracted value, since this change represents the total added distortion due to the cold-work.

	Cu	Ag	Ni	Fe	Mo
Contraction (per cent)	0·06	0·03	0·07	0·05	0·05
Expansion (per cent)	0·27	$0·04_5$	0·13	0·10	0·10
Purity of metals (per cent)	99·999	99·999	99·97	99·96	99·95

§ 3. CRYSTALLINE STRUCTURE AND STRESS/STRAIN RELATIONSHIPS

The mechanism of external strain by progressive dispersal of the grains into crystallites of a lower limiting size has recently been studied in relation to systematic stress/strain measurements; these bring out the next point that the response of the crystalline structure to an applied stress depends essentially on the manner and particularly on the speed of application of the stress.

It may be useful to refer first to the standard response of the structure as given by a specimen subjected to a slowly increased static stress. Up to the primitive yield point there are minor changes only; at the yield a dissociation of the grains into crystallites of widely differing orientations abruptly sets in on an extensive scale; in the plastic range the process continues slowly up to the fracture stage,

when the changes become accelerated. This latter structure of the grains will be described by the term "dispersed crystallite formation" in order to distinguish the condition from the very different structure of the grains in the initial annealed state, or in the elastic range, where the crystallites either are not formed at all or have, to within a degree or two, the same crystallographic orientation as the parent grains, being in consequence practically indistinguishable as far as the x-ray reflections are concerned. The physical significance, therefore, of the primitive yield is that it marks the transition point to the dispersed crystallite formation. This transition is irreversible so that if a specimen is taken through a slow cycle of stress, which is symmetrical in tension and compression, then the internal breakdown occurs as soon as the stress in the first half of the cycle exceeds the yield point, and is retained although the cycle may be applied in such a way as to leave no final external deformation, the change in one half being cancelled by that in the reverse half of the cycle.

Now it is found that if the above type of cyclic stress is applied at a high frequency, then the transition to the dispersed crystallite formation is completely suppressed, although the maximum stress of the cycle employed might very considerably exceed the value of the primitive yield stress in the static test. Perhaps an illustration may be reproduced from some work with Mr P. L. Thorpe on an annealed α-brass of which the primitive yield stress in static tension was 4·8 tons/sq. in., the breaking stress 20 tons/sq. in., and the fatigue limit ± 5 tons/sq. in., the latter indicating that the application of a number of cycles of stress greater than the cycle ± 5 tons/sq. in., tension-compression, would ultimately produce fracture by fatigue. The mode of working was to build up a given cycle in steps of ± 2, ± 3, ... tons/sq. in. so that the amplitude of the strain could be measured at each stress, the frequency of the stress cycles being 2200 cycles per minute throughout. The maximum stress cycle was then maintained for as large a number of cycles as could be applied without precipitating a fatigue crack, and the cyclic stress finally removed, also in steps. The amplitude of the strain was then found to be a linear function of the amplitude of the stress, with the same slope as the elastic portion of the standard *static stress/strain* curve up to the maximum of the cycle; this completely confirmed the inference from the x-ray tests that, with the suppression of the dispersed crystallite formation, the primitive yield point also was suppressed and the original elastic range extended to the maximum stress employed. The striking extent of this effect is shown by figures 7 and 8, the former after a static load (or slow cycle) of 9 tons/sq. in. and the latter after 3×10^4 cycles at ± 9 tons/sq. in. Actually, there appears to be no reason why the elastic range should not be extended in this way up to the breaking stress and a ductile metal thus fractured in a brittle manner without prior plastic deformation.

The obvious interpretation of the above effect is that, owing to the high frequency of test, the stress exceeds the primitive yield point for so short a time in any one cycle that the crystalline structure is not given sufficient time to break down. This time lag raises interesting issues in connexion with the finite time

required for the effective propagation of a slip movement. But perhaps a more important point is the subsequent observation that the inhibition of the transition to the dispersed crystallite formation is permanent. This was proved readily in the work referred to by x-ray photographs taken after the application of increasing static loads to specimens which had first been subjected to cyclic treatment in the above manner, and also by obtaining a subsequent *stress/strain* curve in the usual way; both methods showed that the new primitive yield had been raised to the order of the maximum of the previous stress cycle involved. The metal is thus permanently hardened, virtually as a result of purely elastic strain.

The last observations led to detailed x-ray examination of the hardened state. In a previous research with Dr H. J. Gough on fatigue failure of steel, it had been shown that under cyclic stresses of the above type the initially sharp reflection spots did exhibit a slight but definite diffusion above the fatigue range. Such a change in the α-brass will be noted on comparison of figure 8 with figure 9, which is from the same material in the initial condition. In view of the later observations of lattice strains in cold-worked metals, the same tests were applied to the above types of strain-hardening. These gave the positive result that despite the absence of crystallite formation, permanent strains were built up within the atomic lattice, altering the lattice spacings during the progress of the cyclic test, and these were similar in nature and magnitude to the changes already described in the previous section.

The type of experimental approach described above indicates clearly that there is little if any relation between the process of strain-hardening (as given by the shape of the *stress/strain* curve) on the one hand and, on the other, the response of the internal crystalline structure in respect of the crystallite formation brought out by the x rays, or the external plastic deformation of a metal as observed by mechanical measurements.

§ 4. METALLOGRAPHIC SLIP AND CRYSTALLITE FORMATION IN SINGLE CRYSTALS

Finally it may be of interest to refer briefly to a recent research with Mr W. J. Clenshaw correlating x-ray observations on the dispersal into crystallites with the appearance of slip, as shown by the metallurgical microscope, using large aluminium crystals on which it was found possible to prepare a polished surface suitable for both x-ray and metallographic examination. Under static stress, where there is no appreciable elastic range, the dispersal occurs at once, orientations varying by as much as 20 to 30° being quickly reached even when the slip is taking place in one direction only so that the slip lines are parallel; this shows that the sections of crystal between the slip lines must elongate by considerably different extents under a given stress in order to produce the observed relative variations in crystallographic orientation (without bodily rotation), and to provide the independently reflecting crystallites. Under cyclic stress, with mean stress zero so that no resultant plastic deformation occurs, it is possible by employing high frequency to produce quite dense parallel slip of this type without causing any change whatever in the

x-ray pictures; in this case the sections must deform uniformly so as to retain their initial crystallographic orientations: at the same time the deformation becomes virtually elastic. But if, in the cyclic stressing, the stress distribution is such as to bring into operation more than one slip direction at the same time, producing the characteristic criss-cross slip, then the dispersed crystallite formation again appears in the x-ray photographs: this arises presumably because of local plastic deformations produced by the interference of the various directions.

These points may perhaps serve to indicate the main features of the results obtained by combination of the mechanical and metallographic tests with precision x-ray methods, and some outstanding points requiring consideration in any full theoretical treatment of deformation of metals.

LATTICE DISTORTION IN COLD-WORKED METALS

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ABSTRACT. Measurements of the intensities of x-ray reflections from cold-worked metals indicate that in this respect the lattice distortion resembles a frozen heat motion. Experiments by Hengstenberg and Mark, Boas, Brill, Fricke and his collaborators are quoted in addition to those by the writer. It is shown that with filed powders of Cu, Ni and Rh, the intensity effect decreases in this order.

Measurements of the widths of the reflections from Cu, Ni and Rh, particularly rhodium, are discussed in relation to various theories to account for the broadening of x-ray reflections and it is shown that the most satisfactory explanation appears to be one in which it is supposed that the mean lattice parameter varies from one crystallite to another. It is also shown that the broadening increases in the order Cu, Ni, Rh.

The question why an increase in the intensity effect is accompanied by a decrease in the broadening of the reflections and the relation of these phenomena to the cohesional properties of the metals is briefly considered.

§ 1. INTRODUCTION

The purpose of this paper is to discuss the information obtainable from recent experiments on the intensities and widths of x-ray reflections from worked metals as to the nature of the distortion produced by cold working. The experiments have been carried out with micro-crystalline metals, mainly in powder form, with a crystal size sufficiently small (of the order of 10^{-4} cm. or less) to give continuous lines in the x-ray photographs. When measuring the intensities of reflections it is desirable that the crystallites shall have a random orientation in the specimen and this is most easily obtained with finely powdered metals.

§ 2. THE INTENSITIES OF REFLECTIONS FROM WORKED METALS

Among the earlier experiments may be mentioned the work of Hengstenberg and Mark[13] who examined molybdenum, tantalum, tungsten and duralumin. They considered that at least part of the distortion consisted of an effectively random displacement of the atoms which would produce a lowering of the reflected intensities similar to that produced by heat motion in a lattice. This is shown particularly well by their results for duralumin; they compared the intensities from duralumin which had been heated to 500° c. and quenched in water, 3 and 24 hr. respectively after quenching, with the corresponding intensities from fully annealed duralumin. No change was detected either in hardness or in x-ray intensity 3 hr. after quenching, but after 24 hr. the hardness had reached a maximum and the intensities had decreased in the manner shown in figure 1, which reproduces the results of Hengstenberg and Mark. To describe this effect, Mark introduced the term "frozen heat motion".

This idea was further tested by the writer and F. W. Spiers[4] using fine powders of filed copper and nickel. By means of a specially designed camera[6], the intensities from the filed powders were compared directly with the corresponding intensities from chemically prepared powders of the same metals which were considered to be

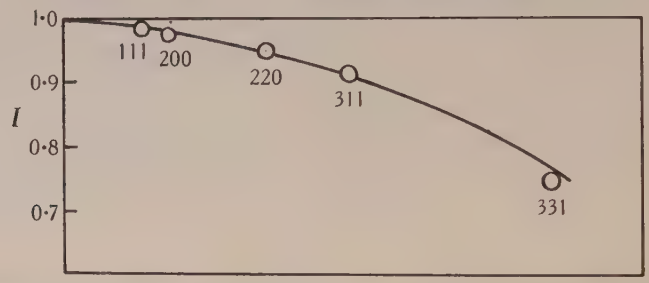

Figure 1. Intensity of reflections from duralumin 24 hr. after quenching, relative to intensity immediately after quenching, as given by Hengstenberg and Mark, *Z. Phys.* **61**, 435 (1930).

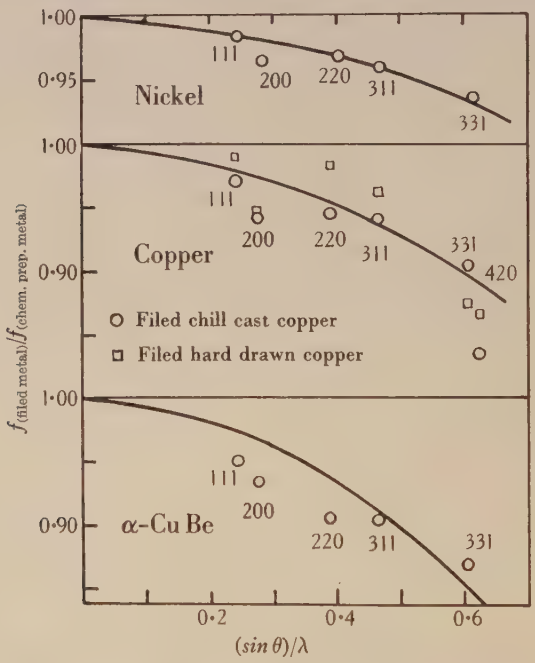

Figure 2. Ratio of scattering factors, f, from filed and chemically prepared metals; the full curves are calculated on the assumption that the atomic displacements resemble a "frozen heat motion".

free from any distortion; the latter were subsequently measured in absolute units by comparison with reflections from aluminium powder. Figure 2 shows the ratios of the scattering factors for the filed and chemically prepared powders plotted against $(\sin\theta)/\lambda$; these values are obtained directly from the ratios of the observed intensities:

$$\frac{f_{\text{(filed metal)}}}{f_{\text{(chemical powder)}}} = \left\{\frac{I_{\text{(filed metal)}}}{I_{\text{(chemical powder)}}}\right\}^{\frac{1}{2}}.$$

The full curves are calculated on the assumption that the atomic displacements in the distorted metal are effectively random and resemble a "frozen heat motion". If $\overline{u^2}$ is the mean square displacement, then

$$\frac{f_{(\text{filed metal})}}{f_{(\text{chemical powder})}} = e^{-M}, \quad \text{and} \quad M = \frac{8\pi^2}{3}\overline{u^2}\left(\frac{\sin\theta}{\lambda}\right)^2.$$

Similar results were obtained with a filed powder of a CuBe alloy in the α-phase[5] (see figure 2).

Experiments of this type have subsequently been carried out by Boas[1] on filed and annealed powders of gold, and by Brill[3] on powders of filed iron, and carbonyl iron before and after various heat treatments. In these experiments, however, only *relative* intensity measurements were made, and the experimental arrangements did not permit of a *direct* comparison between the two powders; the interpretation of the results is therefore less certain, but on the whole they confirm the conclusion stated above.

Table 1. Values of $[f_{(\text{distorted metal})}/f_{(\text{undistorted metal})}]$ for copper, nickel and rhodium

Metal	$[f_{(\text{distorted metal})}/f_{(\text{undistorted metal})}]$	
	$(\sin\theta)/\lambda = 0{\cdot}5$	$(\sin\theta)/\lambda = 0{\cdot}6$
Copper	0·92	0·89
Nickel	0·95	0·93
Rhodium	0·96–1·00	0·97–1·00

The importance of absolute measurements is shown by the results obtained in a recent investigation of lattice distortion in filed rhodium[7]. The lower order reflections from the filed powder and from a chemically prepared powder indicated marked extinction in both powders. The uncertainties introduced in attempting to correct for the extinction render the final results for rhodium less precise than for copper and nickel, but for reflections occurring at values of $(\sin\theta)/\lambda$ greater than about 0·5 the correction is small and the results obtained provide useful information.

The results for copper, nickel and rhodium[8] are compared in table 1 where values of the ratio of f for the distorted and for the undistorted metals are given for $(\sin\theta)/\lambda$ equal to 0·5 and 0·6. The values given for rhodium are obtained after correcting for extinction. It is clear that the effect of lattice distortion in reducing the reflected intensities increases as we go from rhodium through nickel to copper. Since rhodium is the hardest and copper the softest of these metals, there is perhaps a significant relation between the distortion of the metals and their cohesional properties.

The results obtained by Boas[1] for gold are consistent with this idea since they are of about the same magnitude as those for copper; the cohesional properties of the two metals also are similar, the melting points, for example, being 1083° C. for copper and 1063° C. for gold. Unpublished measurements by the writer for silver also agree qualitatively with this view; silver is a softer metal than copper and the intensities of high-order reflections appear to be reduced by distortion at

least as much as the copper reflections. It is difficult, however, to deal quantitatively with the results for silver owing to the presence of large extinction.

In table 2 are given values of $\sqrt{u^2}$, the r.m.s. atomic displacement calculated from the expression for M given above, and the values for gold and iron obtained by Boas[1] and by Brill[3] are also included. By applying the well-known Debye-Waller formula for the effect of temperature on x-ray intensities, Boas has calculated the equivalent temperature of the "frozen heat motions" and hence the energy of the distorted lattices; these data are also collected in table 2.

Table 2. Data relating to lattice distortion in filed metals, assuming the distortion to be of the nature of a "frozen heat motion"

Metal	Crystal structure	$\sqrt{u^2}$, in A	Energy, cal./g. (Boas)
Copper	Face-centred cubic	$0{\cdot}10_6$ (B. and S.)	7·4
Gold	,, ,,	$0{\cdot}11_9$ (Boas)	3·5
Nickel	,, ,,	$0{\cdot}08_3$ (B. and S.)	6·4
Rhodium	,, ,,	Less than 0·08 (B. and R.)	—
Iron	Body-centred cubic	0·12 (Brill)	—

B. and S., Brindley and Spiers. B. and R., Brindley and Ridley.

It is of interest to compare the energies given in table 2 with values obtained by direct calorimetric methods. In experiments on pure annealed copper subjected to rapid twisting, Taylor and Quinney[18] have found that the maximum absorbed energy is 1·149 cal./g. and the corresponding figures for annealed and for carburized mild steel are respectively 1·267 and 0·660 cal./g. These figures are appreciably smaller than those in the final column of table 2 but they are roughly of the same order of magnitude. Boas[1] has suggested that if, instead of the atoms being displaced purely at random, groups of atoms were similarly displaced, then the energy would be less than that calculated for a purely random displacement.

Experiments by Fricke and his collaborators[11] also point to a connexion between the intensity of x-ray reflections and internal energy due to lattice distortion. They find that substances, such as zinc oxide, copper, iron, etc., have a greater heat of solution when prepared by chemical reduction at low temperatures than when prepared at higher temperatures, and also give a correspondingly reduced intensity of x-ray reflection. Assuming that the decrease of x-ray intensity is due to distortion of the type discussed above, they calculate the mean square atomic displacement and hence the energy associated with the distortion. This energy they find, in general, to be in agreement with the increased heat of solution. Some of their results for copper and iron are set out briefly in table 3.

The close agreement between the energies obtained in the two ways is indeed striking. The energies given in table 3 are considerably greater than in table 2, being respectively 51 cal./g. for copper and 25 cal./g. for iron; for both metals, however, the powders prepared by low-temperature reduction were strongly pyrophoric.

The writer and G. H. Atkinson are at present investigating the intensities of reflections from copper powders prepared by chemical precipitation at various temperatures. There is a marked decrease in the intensities reflected from powders precipitated at low temperatures, but it is not possible yet to say whether the results indicate a random atomic displacement.

Table 3. Data relating to lattice distortion in copper and iron, as given by R. Fricke and collaborators

	Heat of solution, in k.-cal./g. atom	
	Copper*	Iron†
Prepared by low-temperature reduction	48·3	$23{\cdot}7_2$
Prepared by high-temperature reduction	$45{\cdot}1_5$	$22{\cdot}2_9$
Excess energy of low-temperature product	$3{\cdot}1_5$	$1{\cdot}4_3$
From x-ray data, r.m.s. atomic displacement	0·26 A.	$0{\cdot}07_6$ A.
Energy of distortion, from x-ray data, k.cal./g. atom	3·24	1·43

* R. Fricke and F. R. Meyer, *Z. phys. Chem.* A, **183**, 177 (1938).

† R. Fricke, O. Lohrmann and W. Wolf, *Z. phys. Chem.* B, **37**, 60 (1937); B, **39**, 476 (1938).

§ 3. THE WIDTHS OF X-RAY REFLECTIONS FROM WORKED METALS

It is well known that when most metals are cold worked the widths of the x-ray reflections are broadened, but although the effect has been extensively studied, the cause of the broadening for the most part still remains obscure. It is not intended to make a general survey but to restrict the discussion to measurements made on the same powders as were used for the intensity measurements described in § 2.

Two questions will be specially considered: (1) What change takes place in the crystal lattice causing broadened reflections? (2) What connexion is there between the broadening and the intensity effect?

With regard to question (1), three kinds of explanation have been suggested, (*a*) that the broadening is produced by a very small crystal size, $\sim 10^{-6}$ cm., (*b*) that it is due to ghost reflections adjacent to the main reflections arising from *periodic* displacements of the lattice, (*c*) that the mean crystal parameter varies slightly from one crystallite to another.

In the experiments on Cu, Ni and Rh already mentioned, filed rhodium was found to give particularly broad lines; the widths were therefore studied in detail for five different radiations, the $K\alpha$ radiations of Zn, Cu, Ni, Co and Fe. An outstanding feature of the results is that when the widths are plotted against the angle θ, they fall on or near a single curve (see figure 3), and such deviations as occur cannot be correlated with the wave-lengths. These results will be considered briefly in relation to (*a*), (*b*) and (*c*) above.

(*a*) Scherrer[17] first gave the following expression for the angular width B of reflections from crystals of size L:

$$B = b + 2\lambda \sec\theta \, (\log_e 2/\pi)^{\frac{1}{2}}/L,$$

where b is a constant. It follows that for any particular value of θ, the width B should vary linearly with λ. A separation of the widths measured with different radiations would therefore be expected when plotted against θ. The theory has

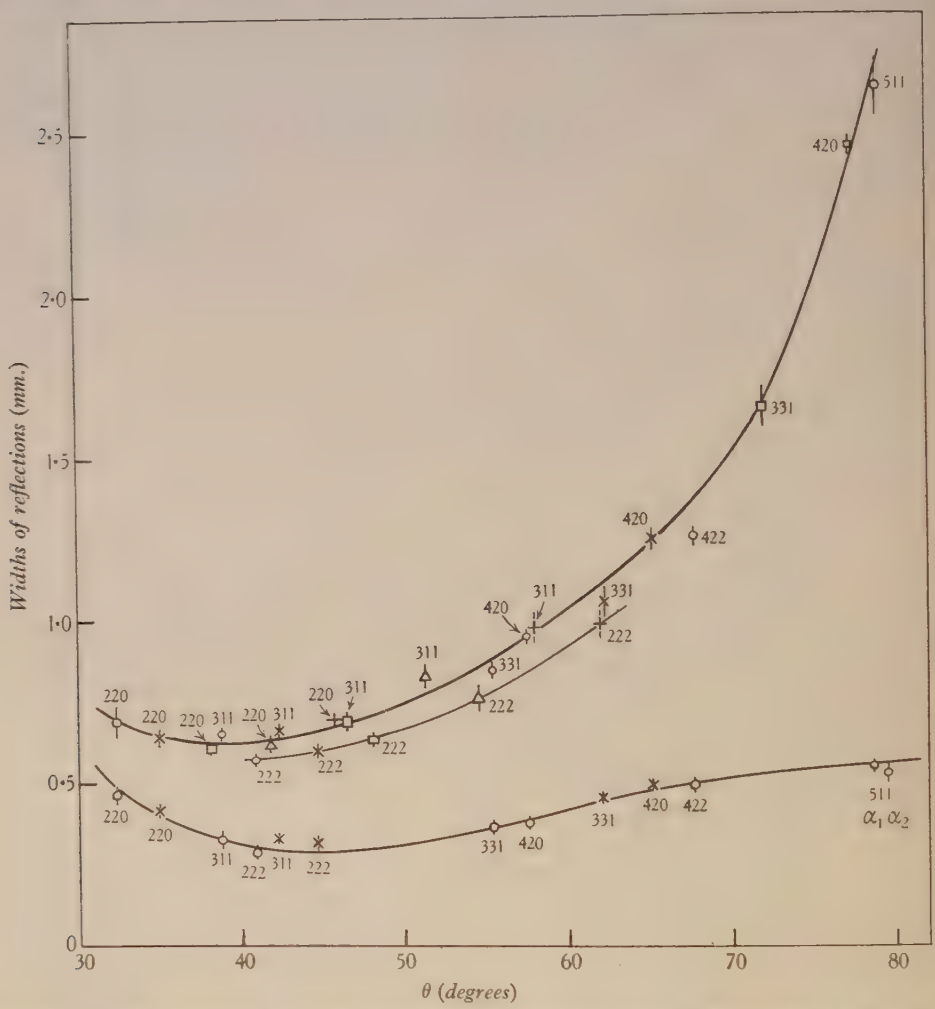

Figure 3. Laue widths of reflections, after correction for $\alpha_1\,\alpha_2$ separation, plotted against θ. The lower curve is for chemically prepared rhodium powder, the upper curves are for the filed powder. Except for the 222 reflections the widths from the filed powder lie on or near the mean curve; a slightly lower curve passes through the points representing the 222 reflections. The symbols indicate the radiations employed: ○, zinc $K\alpha$; □, nickel $K\alpha$; ×, copper $K\alpha$; △, cobalt $K\alpha$; +, iron $K\alpha$. From G. W. Brindley and P. Ridley[7].

subsequently been treated more fully by v. Laue[16] and his results have recently been applied by Kochendörfer[15] to the case of a flat powder layer at the centre of a cylindrical camera, which was the arrangement used in the rhodium experiments. This more complete treatment also indicates that there should be a well-marked separation of the widths according to the wave-length of the radiation when the

widths are plotted against θ. This is entirely contrary to the observed results and indicates that the broadening cannot be due to a small crystal size.

A further point is that the mean crystal size would have to be as small as about

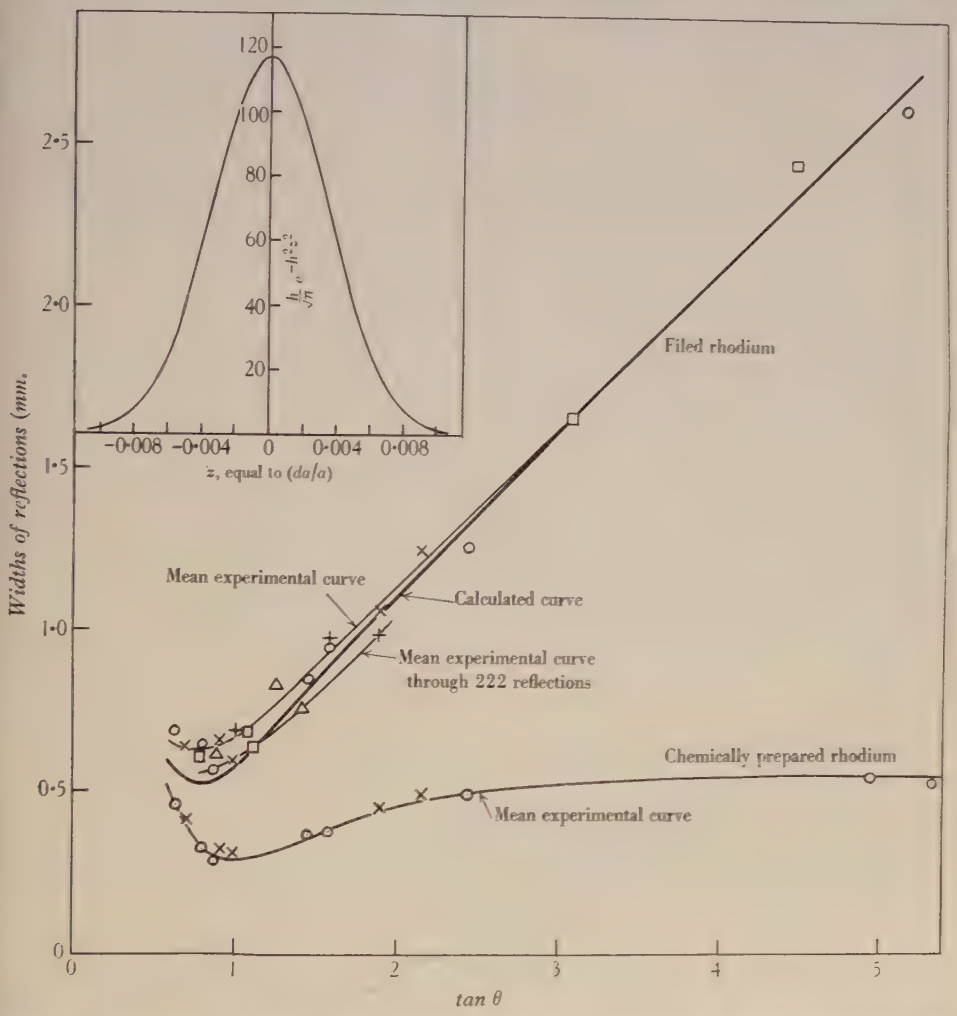

Figure 4. Reflected widths from filed and chemically prepared rhodium plotted against tan θ. The heavy curve running through the observations for the filed metal is calculated on the assumption of a Gaussian distribution of the lattice spacing about the normal mean value. The distribution is shown in the inset. From G. W. Brindley and P. Ridley[7].

90 A. in order to produce broadening of the observed magnitude, and with such small crystals primary extinction would be negligible. There is, however, a relatively large extinction effect and the crystal size estimated in this way is of the order of $6{\cdot}5 \times 10^{-5}$ cm. It appears quite impossible to reconcile the large extinction effect with a crystal size sufficiently small to cause broadening of the observed magnitude.

(*b*) The theory of broadening due to ghost reflections* has been treated by Dehlinger[10] and by Boas[2]. It requires in the first place that the distortions shall be of a *periodic* nature. Secondly, in order that the ghost reflections shall lie adjacent to the main reflections and be of appreciable intensity, it is necessary that the distortion shall follow a simple cosine law. Dehlinger considered in detail distortions of a cosine type while Boas examined a type of distortion in which blocks of the lattice are displaced normal to the reflecting planes at regular intervals; Dehlinger's analysis indicated a broadening of the reflections, but the type of distortion considered by Boas gave no appreciable broadening. This difference is analysed by Boas by means of Fourier analysis and he shows that as the distortion

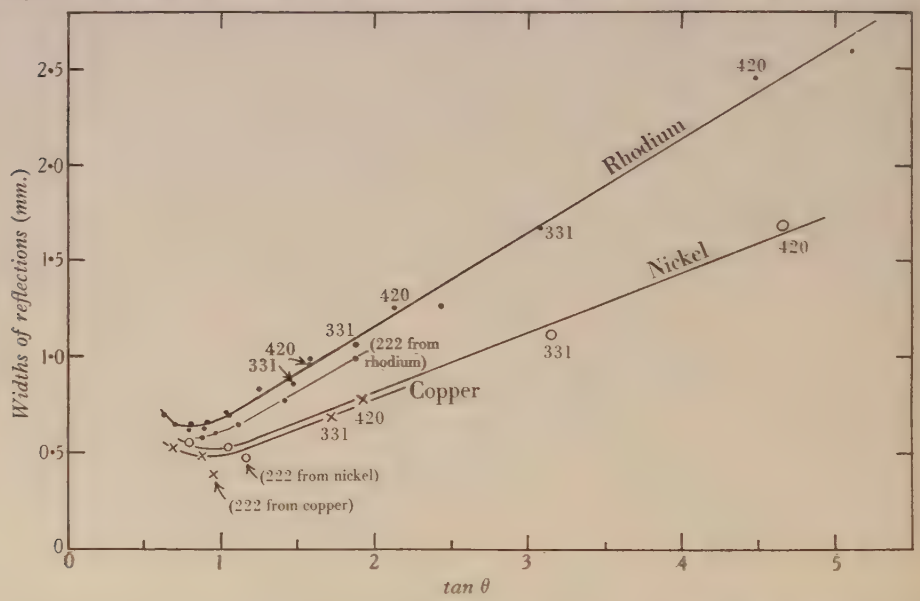

Figure 5. Widths of x-ray reflections from filed powders of copper, nickel and rhodium, plotted against tan θ for the following radiations. Rhodium, $K\alpha$ radiations of zinc, copper, nickel, cobalt and iron; copper, $K\alpha$ radiation of zinc; nickel, $K\alpha$ radiation of copper. From G. W. Brindley and P. Ridley[8].

becomes more complex, i.e. requires more Fourier terms to describe it, the lattice ghosts become rapidly weaker and more diffuse*. In consequence, an appreciable broadening of the reflections will occur only if the distortion approximates closely to the simple cosine type. This seems so highly improbable in practice that it is almost sufficient evidence in itself to show that the cause of the broadening cannot be due to ghost reflections; this was, in fact, the conclusion finally arrived at by Boas. We have, however, examined the results for rhodium to see if they can be explained by means of a distortion of a cosine type, but without success[8].

(*c*) The possibility that the broadening may result from a variation in the

* *Note added in proof*, 17 *July*. Since this was written two papers by Kochendörfer and by Dehlinger have appeared[20] criticizing the analysis given by Boas[2] and discussing in more detail the type of broadening resulting from distortions of a periodic type; it appears that the conclusions drawn by Boas regarding the type of line-broadening resulting from complex lattice distortions may be invalid.

mean lattice parameter from one crystallite to another is widely referred to in the literature (e.g., W. A. Wood[19], Caglioti and Sachs[9], Haworth[12], and others), but the idea does not appear to have been extensively tested. It follows from the Bragg equation that any change da in the mean crystal parameter will change the angles of reflection by an amount $-\tan\theta\, da\, a$ and the reflected lines on a photographic film of radius R will be displaced a distance

$$dx = -2R \tan\theta\, da/a.$$

The shape of a broadened line will then depend on the distribution of $da\, a$, on $\tan\theta$, and also on the focusing properties of the camera. Assuming that da/a is distributed according to a Gaussian law, we have, for the probability dp that da/a will lie in a small range between z and $(z+dz)$, the expression

$$dp = (h\sqrt{\pi})\, e^{-h^2 z^2} dz.$$

Allowance for the focusing properties of the camera is made by measuring reflections from chemically prepared rhodium. We can then calculate for each value of θ what the widths of the broadened lines will be for any particular value of the constant h in the distribution function. Throughout the calculations allowance was made for the separation of the $\alpha_1\alpha_2$ components of the radiation on the basis of the method developed by F. W. Jones[14].

Figure 4 shows the measure of agreement obtainable between the observed and calculated widths of the rhodium reflections. A similar agreement has been obtained for copper and nickel. The widths of the reflections from filed copper and nickel are compared with the rhodium results in figure 5. The r.m.s. variation in lattice parameter, $(\overline{z^2})^{\frac{1}{2}}$, where $z = da\, a$, has the following values for the three metals:

Rhodium	0·00431
Nickel	0·00223
Copper	0·00205

§ 4. A COMPARISON OF THE WIDTHS AND INTENSITIES OF REFLECTION FROM WORKED METALS

In § 2 it is shown that the decrease of reflected intensity increases in going from rhodium through nickel to copper; in § 3 it is shown that the widths of the reflections increase in the reverse order. This is also the order of the metals when grouped according to hardness. The question then arises why an increase in the intensity effect is accompanied by a decrease in the broadening, and what is the connexion between these phenomena and the cohesive properties of the metals.

The following tentative suggestions are put forward with the utmost reserve. In the first place it is seen that the intensity effect decreases in going from the softest metal, copper, to the hardest, rhodium. This may be taken as an indication that as the hardness of the metal increases, the magnitude of the atomic displacements decreases. A somewhat different view is that the atomic displacements probably originate at the slip planes when a metal is worked and that slip occurs either more frequently or more extensively in the softer metals, so that we might expect that the softer the metal the greater would be the fraction of displaced atoms, and therefore

the greater would be the intensity effect. We have next to attempt to link up these ideas with the variation in the mean lattice parameter from one crystallite to another which seems to be indicated by the broadening of the reflections. If we suppose that the more readily slip occurs in a metal the less will be the chance of there being any appreciable change in the mean parameter, then the softest metal, copper, will show the smallest broadening of the reflections, and rhodium, the hardest metal, will show the largest broadening. These ideas are admittedly tentative and are put forward in the hope of provoking comment from workers interested in the subject from other standpoints.

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THE MECHANICAL EFFECTS OF INTER-CRYSTALLINE BOUNDARIES

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ABSTRACT. The effect of a single crystal boundary on the critical shear strength of a metal is investigated.

It is well known that the mechanical properties of a metal are greatly influenced by the size of the constituent crystals of the sample under test. An extreme example is the difference between a single crystal of copper, which in the form of a rod of half an inch diameter can be bent in the hands, and a polycrystalline rod of copper of the same dimensions. Although the existence of this effect is well recognized, its explanation is by no means clear, and it is the object of this paper to discuss the available evidence.

The effect of crystal size on the mechanical properties may be considered as resulting from the presence of crystal boundaries, and this leads to a distinction between effects due to the mechanical properties of the boundary itself, and effects due to the fact that two crystals of different orientations are in close proximity at any boundary. These two possible effects will be referred to as direct and indirect respectively. Another possibility that must not be overlooked is that the properties of the crystals themselves depend on their size. It appears probable that this effect will only be important when the crystal size is very small, e.g. when the linear dimensions are of the order of 10^{-4} cm., because that is the order of size at which a change in the lattice constants is believed to commence. This effect will not be discussed further here because it does not lie within the scope of this paper.

As far as can be seen from existing data, the general effect of grain size is the same in alloys in which one phase only is present in the solid, and in relatively pure metals. The discussion will therefore be restricted to the latter case. It is realized that the effects of the crystal boundaries may be quite different in cases where a second phase is present in small quantities, as in some of the alloys studied by Homer and Plummer[1]. Where minor constituents are present in solid solution, such considerations do not apply.

Before considering in detail the relevant experimental work, it is necessary to point out that numerous direct investigations of the effect of grain size, while having the greatest practical interest, cannot be used as the basis for fundamental considerations. There are several reasons for this, of which the most important is that when a variation in grain size is brought about by mechanical and thermal treatment, there is a likelihood of some other change also occurring, such as the introduction of internal strain, the production of a preferred orientation, a change in shape of the grains, or a change in the distribution or equilibrium of minor con-

stituents. Unless it can be shown, therefore, that a series of samples differs only in the size of the crystals, it cannot be regarded as useful from the present point of view. A second reason for not considering the work that has been done on polycrystalline metals is that the majority of mechanical tests are very difficult to interpret in terms of recognizable physical characteristics. Further, it may be necessary to distinguish between absolute grain size and relative grain size, i.e. the size of the crystals expressed in relation to the dimensions of the test piece.

A more promising approach, therefore, is to consider the results of experiments in which the number of grain boundaries is small, and to study the way in which the presence of one or more boundaries causes the behaviour of the specimen to differ from that of a single crystal. Experiments on single crystals have shown that the distortion of a crystal follows certain definite laws, which can be summarized as:

(1) Shear takes place in a crystallographic direction of a type which, in the case of a given metal at a given temperature, is fixed.

(2) Shear usually takes place in planes of definite crystallographic type.

(3) Shear takes place in one of these directions when the shear stress in that direction reaches a value that is characteristic of the material and its previous history.

(4) The critical shear stress is independent of the tension in a direction perpendicular to the shear direction.

Our first step is to examine the evidence regarding the effect of intercrystalline boundaries on these conditions. The experimental side is complicated by the fact that at least two crystals must be present in a specimen containing an intercrystalline boundary. On this account, the relevant experimental investigations are of two kinds, namely, those in which the effect of a boundary on the direction of slip is investigated, and those in which the effect of a boundary on the critical shear stress is determined. In the former class are the investigations of Gough and his collaborators[2] on the effects of alternating torsional stresses on aluminium specimens containing a few crystals only. In these investigations the orientations of the crystals were determined by x-ray methods, and the shear stresses in the various possible slip directions were calculated. The actual planes in which slip took place were observed by microscopical examination of the surface, and it was found that the presence of the boundaries did not invalidate the law deduced from single crystal work, that slip takes place along the slip direction in which the resolved shear stress is greatest, i.e. in which the critical shear stress is first exceeded. In other words, glide takes place in any one crystal in the same directions and on the same planes as it would if the specimen consisted of that crystal only.

The geometrical characteristics of slip, therefore, are not disturbed by the presence of a boundary except, possibly, in the immediate vicinity of the boundary. At the same time, there is no doubt that the critical shear stress is raised by the proximity of a boundary, and that the amount of slip that takes place is decreased. The experiments of Chalmers[3] on this subject were directed to the investigation of the extent to which this increase of critical shear stress is affected by the angle between the crystallographic axes of the two crystals concerned. The test pieces

consisted of cylindrical specimens of tin which contained two crystals with their boundary running the whole length of the specimen in a plane containing its axis. In order to ensure that a given tension in the specimen corresponded to a definite shear stress in any set of slip planes, the crystallographic axes of the crystals were in all cases similarly inclined to the geometrical axis of the specimen. The *c* axis was in each case perpendicular to the axis of the cylinder, and this allowed the angle between the *c* axes of the two crystals to have any value from 0° to 90°. The method of testing was to measure the stress required to cause a definite small increase in length. It was found that this tension varied in a regular and approximately linear way with the angle between the *c* axes, the extrapolated value for 0° agreeing with the value found for single crystals. The variation of tension between the two extremes was considerable, the values being 400 g.wt./mm.^{2} for a single crystal to 650 g.wt./mm.^{2} for a specimen in which the angle was 90°. Thus the presence of one boundary was able, under suitable conditions, to raise the yield stress by 60 per cent over the value characteristic of a single crystal. This seems to suggest that there is no specific boundary layer or material with a definite mechanical effect of its own, and that the increased yield stress is due to a secondary effect.

It may be stated, therefore, that crystal boundaries, when formed in a relatively pure metal, do not themselves modify the stress-strain characteristics of the crystals; but that the proximity of a second crystal raises the stress required to initiate slip to an extent that depends on the angle between the axes of the crystals, without altering the planes or directions that are effective.

It does not seem possible, however, that this conclusion can be applied to the crystals of a polycrystalline aggregate, in which the crystals are much smaller than those discussed above, and are completely surrounded by other crystals except when they happen to lie in the surface layer.

It was pointed out by Taylor[4] that the crystals of such an aggregate must deform, under tension, so that all dimensions parallel to the direction of the stress shall increase in a given ratio while all transverse dimensions decrease by half this amount. If this were not the case, the shapes of the crystals would be so changed that their surfaces would no longer fit after deformation. This would involve great reduction of strength and the formation of spaces between the crystals that are precluded by microscopic observation and by density measurements. Taylor showed, moreover, that in a metal such as aluminium, which crystallizes in the face-centred cubic system, a combination of slip in five of the twelve possible directions is in general necessary to produce the required type of deformation. It follows, therefore, that the resolved shear-stress law cannot be regarded as applying directly to the crystals of a polycrystalline aggregate. That is to say, the applied stress and the orientation of a given crystal cannot be regarded as the only two factors that control the choice of slip planes and slip directions; the orientations of the neighbouring crystals must also be taken into account. One can, however, regard the shear-stress law as applying, and draw conclusions as to the internal distribution of stress that is necessary to cause the five directions of slip to

operate. In this way, it is permissible to regard the first plastic deformation as that which obeys the resolved shear-stress law. The redistribution of stress brought about by this primary slip will increase the resolved shear-stress in other directions or other planes so that the second glide on a second plane takes place. An extension of this process would lead to the practically simultaneous operation of the required five directions of slip, each process being subject, in detail, to the resolved shear-stress law. It follows that considerable internal forces must act through the crystal boundaries in directions inclined to the direction of the applied force as well as along it, and that the shear and tensile strengths of the intercrystalline boundaries must be high.

It must be concluded that the characteristics of glide as determined for single crystals are modified very much more by the presence of a number of adjacent crystals than by the presence of one only. There is some evidence, indeed, which indicates that the type of deformation established for single crystals does not always take place for the crystals in a polycrystalline mass. The experiments of Andrade and Chalmers[5] on the variation of the specific resistance of cadmium during plastic flow under constant stress showed that the flow exhibited two stages, in the first of which the length could be represented as increasing with the cube root of the time, and in the second, directly with the time. In the first stage, the specific resistance decreased in a manner that suggested that the axes of the crystallites were rotating, as would be the case during glide. In the second stage, no further change in specific resistance took place, and this indicated that glide in the crystals had ceased. Both these conclusions were confirmed by the x-ray investigations of Gibbs and Ramlal[6]. The second or constant-resistivity stage generally persisted throughout a large amount of extension, and the exact nature of the flow taking place does not seem to have been settled. Two facts are evident; in the first place, glide does not take place in the ordinary way as established for single crystals. If it did, further rotation of the axes would be inevitable in the case of a hexagonal metal such as cadmium in which there is only one possible type of glide plane. Secondly, it is impossible that each crystal should retain its external shape unchanged during a 20 per cent extension of the specimens, because the relative positions of the crystals would change so as to leave large spaces between the crystals. It follows that each crystal changes its shape in a regular and symmetrical manner, so that the conformity of the boundaries is maintained; that this cannot result from glide on the ordinary hexagonal planes of a metal like cadmium follows from the work of Taylor that has been discussed above. The conclusion is that after a certain amount of glide has taken place, the ability of the crystal to glide along the permissible planes has decreased to such an extent that this type of deformation no longer occurs. Subsequent deformation must then be of the kind that takes place in amorphous materials, shear occurring in all directions inclined at 45° to the direction of stress. Since this type of distortion has not been observed in any experimental work on single crystals, it seems probable that it is conditioned by the presence of numerous crystal boundaries, and may be possible only when the crystals are completely surrounded by boundaries.

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MECHANISM OF GLACIER FLOW

By M. F. PERUTZ, Cavendish Laboratory, Cambridge*

ABSTRACT. The internal mechanism of glacier flow has been studied by examining the crystal textures of samples of snow and ice from different parts of Alpine glaciers, and by taking strain-measurements within the glaciers themselves. The results show that under the influence of glacier flow *firn*, a compacted snow covering the upper regions of glaciers, is deformed through relative motion of individual ice crystals, whereas the ice which forms the bulk of the glacier yields by crystal deformation and crystal growth on the one hand, and by slip over large thrust planes on the other hand.

Flowing glaciers undergo a continuous process of plastic deformation. They flow faster at their centre than at the sides, and faster at the surface than in their interior. This phenomenon is known as differential movement. Being constituted of ice crystals of hexagonal symmetry (α ice) possessing a well-marked basal glide plane, glaciers offer an excellent means of studying the behaviour of a polycrystalline ionic material under strain. The fact that little use has hitherto been made of this possibility may principally be attributed to the experimental difficulties involved in an investigation of this nature.

The difficulties have mainly been of two kinds: first, to determine quantitatively the strain which a given portion of the glacier is undergoing, and secondly, to study the crystal texture of glacier ice. Mr Seligman and his party, of which I was a member, have been able to overcome these obstacles by choosing the International Research Station on the Jungfraujoch as base of their operations. The facilities available at the Jungfraujoch made it possible for us to bring considerable quantities of scientific equipment to the source of the Aletsch Glacier—the largest ice stream in the Alps—and also to establish a complete low-temperature laboratory at an altitude of over 11,000 ft. for crystallographic work on thin sections of ice.

The first object of our studies was the glacier basin in the vicinity of the Jungfraujoch where the annual accumulation of snow exceeds the loss by melting and evaporation; the basin is therefore called an *accumulation area*. In summer it is covered by a granular compacted snow called *firn*; this consists of crystals measuring between 1 and 3 mm. in diameter and enclosing a considerable volume of air between them. They are formed by repeated melting and refreezing of fallen snow.

While the crystals in fallen snow probably lie in more or less random orientation, optical examination showed that in firn the majority of them are oriented with their hexagonal axes normal to the glacier surface. This preferred orientation was found

* Publication No. 5 of the Jungfraujoch Research Party.

to be due to the recrystallizing process involved in the transition of snow into firn, during which the crystals become oriented with their hexagonal axes parallel to the direction of the temperature-gradient.

Changes in crystal texture in the interior of the accumulation area were followed by taking samples from the walls of crevasses at varying depths. It was found that the preferred orientation is confined to the glacier surface, and as firn several years of age is approached, this gives way to a random distribution of axial positions. The loss of order, however, only takes place in the firn, where, owing to the enclosed air spaces, the crystals are in relatively loose contact, but not in certain bands of clear blue ice interleaving the firn where the crystals are closely packed. It was deduced from these results that the differential movement has a disrupting influence on the loose firn crystals, causing them to turn round and move relatively to one another, while the adhesive forces between the crystals in the *ice bands* are large enough to withstand the stress.

The accumulation area forms but a small part of the glacier. The lower part of the glacier, the *ablation area* or *glacier tongue*, is totally different in appearance. Its crystals are many times larger than those in even the deepest layers of firn, and enclose fewer and larger air spaces which, in contrast to the firn, generally are intracrystalline. As we were able to show, the transition of small-crystalline firn into large-crystalline ice goes on in the absence of any outside supply of melt water. Hence the increase in size can only be achieved by the growth of certain portions of the crystals at the expense of their neighbours. The process of selection by which some crystals grow and others diminish in size was one of the problems confronting us, and was found to be intimately connected with the differential movement in the glacier tongue.

Since the close packing of the crystals in the ice bands had prevented their relative motion, it was evidently improbable that relative motion of the crystals would furnish an explanation of the differential movement in the glacier tongue, where the crystals are often of very complex shape and always closely interlocked. Hence it was to be expected that the ice would either yield by slip along the basal glide planes within the single crystals or that, if yield should be impossible, cracks would develop along which overthrusts might take place.

An example of yield without rupture was found in an ice grotto on the Jungfraujoch at an altitude of 3400 m. Here a column of ice which had originally been straight and vertical became tilted at an angle and had bent under the influence of the differential flow. The deformation had not produced any crack in the column, although it had been at a temperature of -4° C., which is considerably below the pressure melting point. Examination of sections of ice taken from this column showed that all the crystals were oriented with their basal planes parallel to the direction of flow. The majority of them also had their basal planes parallel to the surface of the ice slope above the grotto. (The direction of flow was, of course, parallel to the surface.) It was possible to ascertain that this preferred crystal orientation was not due to a melting and refreezing effect from the surface, and therefore it appears justifiable to attribute it to the effect of plastic deformation.

In an ice grotto at an altitude of 2300 m. where the temperature of the ice was at the pressure melting point, an instance was found where both plastic yield without rupture and slip over a large thrust plane were operative. Stresses which probably were parallel to the glacier surface had caused shear to develop at an angle of 45° to the surface.* A layer of ice which itself remained undistorted was carried over a thrust plane and appeared to exercise a drag on the ice underneath, which in its turn yielded by plastic deformation. The air bubbles in the deformed ice were not spherical, as they usually are in the glacier tongue, but were all squashed into flat ellipsoids whose equatorial plane was parallel to the thrust plane. Since the bubbles were all intracrystalline it was evident that deformation of the single crystals had taken place. The thrust plane itself consisted of a band of large crystals which were free from air bubbles, and a band of very large flat air bubbles above. A thin section cut from the band showed that the majority of the crystals had their basal planes oriented parallel to the plane of the band, i.e. parallel to the plane of shear.

The evidence described above indicates that strain has two effects on ice which is at or near its melting point. First it causes deformation and reorientation of the crystals, and secondly it produces crystal growth. It is not certain whether growth follows or accompanies deformation, but from our results in glaciers and also from the outcome of laboratory experiments on the mechanical strength of polycrystalline ice[1] it appears certain that an increase in the average crystal-size is invariably observed after strain has taken place. Mechanical twinning and recrystallization by the formation of new crystal nuclei, on the other hand, have not been observed. The behaviour of polycrystalline ice thus seems to some extent analogous to that of strained metals, except for the absence of the recrystallization stage whose place is immediately taken by crystal-growth.

It may be suggested as a working hypothesis that deformation and growth in ice are interconnected in the following manner: crystals having the right orientation for yielding to stresses by glide along their basal planes would have a higher energy than others which cannot yield; the former would therefore have a tendency to grow at the expense of the latter by molecular exchange across the crystal boundaries. In glaciers the change in crystal orientation brought about by intracrystalline gliding and the alterations in stress to which the ice is subjected in the course of its flow to the valley would continuously give rise to fresh energy-differences between neighbouring crystals, and to consequent crystal growth. This may explain the abnormally large size of the glacier crystal, referred to above.

Our experimental results made it possible to decide between several schools of thought as regards the internal mechanism of glacier motion. They showed that firn is essentially plastic, and yields to stresses by the independent motion of single crystals or small patches of crystals. Large-scale thrust planes, therefore, do not occur in the firn region. Glacier ice, on the other hand, yields to stresses by deformation and growth of the single ice crystals and, provided the stress exceeds a certain value, also by the formation of large thrust planes. While there is little doubt

* It never was possible to measure stresses in our field work, but only the strains resulting from them.

that differential flow in the firn region is continuous, the slip over thrust planes found in the tongue may be spasmodic, as has been suggested by Chamberlin[2] and others.

A full account of the experiments has been published elsewhere[3].

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DISCUSSION. PART III

Dr E. Orowan. Theoretical conceptions of the structure of strain-hardened crystals often have the drawback that it is difficult to see whether, and how far, the structure proposed can explain the observed increase of hardness. Prof. Bragg's picture of the strain-hardened state, however, permits a rough estimate of the increase of shear strength due to the subdivision of the crystal by surfaces of misfit.

If a crystal glides along a plane, figure 1 *a*, new surfaces 1 and 2 are created. Let x be the relative displacement of the two parts of the crystal, w the width of the crystal in a direction perpendicular to the direction of gliding, and α the surface energy of the glide plane; then the displacement x produces an increase $2\alpha wx$ of the total free surface energy. That is to say, a minimum shearing force $2\alpha w$ is necessary to deform the crystal; if the force acting upon the deformed crystal is less than this, the crystal will, in the course of a sufficiently long time, glide back into its undeformed shape.

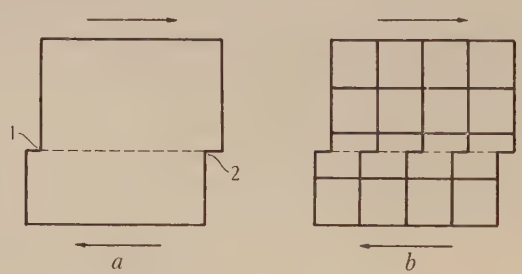

Figure 1.

Let us assume now that the crystal is subdivided by surfaces of misfit, the average distance of which is d, and that gliding takes place between (not along) these surfaces. Furthermore, we assume that the surfaces of misfit are extended by the deformation in the way shown in figure 1 *b*; this is, evidently, the case if the lattice orientation varies from block to block. The number of surfaces of misfit per unit of length being $1/d$, the minimum force per unit of area of the glide plane necessary to produce gliding will be α/d, if α is now the specific surface energy of the surface of misfit. The surface energies of free surfaces of metals are of the order of 1000 erg/cm^2; the specific energy of the internal surfaces is very much lower, and we may assume it to be of the order of 100 erg/cm^2. For the distance d in a heavily worked metal, values between 10^{-4} and 10^{-5} cm. have been proposed as a result of X-ray work, and thus a shear strength between 10^6 and 10^7 dyne/cm^2 or between 1 and 10 kg./cm^2 is obtained for the shear strength due to internal surfaces of misfit. This is of an order not very far from the actually observed increase of shear strength due to strain hardening.

Strain hardening is usually attributed to the difficulty of the propagation of dislocations across surfaces of misfit. This and Prof. Bragg's conception of strain

hardening complement each other, the one looking at the phenomenon from an energetic and the other from a dynamic point of view.

Dr W. G. Burgers. With regard to Dr Wood's and Dr Brindley's papers, I would like to remark that the broadening of the interference lines in Debye-Scherrer x-ray photographs of cold-worked metals must be ascribed to small particle-size or to lattice distortion (consequent upon internal stresses). For tungsten, arguments in favour of the second assumption have been deduced from the fact[1] that the sharpness of the interference lines on photographs of a drawn wire or a rolled foil, as measured by the relation of the intensity of the maximum of the α_1 line to the minimum between the α_1 and α_2 lines, when the specimen was heated at a definite temperature, increased within a relatively short time to an end value, which, within the accuracy of the measurements, remained approximately the same on further heating. This end value was higher, the higher the temperature of heating, the temperature being chosen so low that no visible re-crystallization occurred.

This behaviour seems different from the gradual increase in line-sharpness which one would expect to occur if increase in crystal size (domain size), due to the heating, were the cause of the phenomenon. The behaviour resembles closely the way in which other physical properties alter as a function of the time of heating at different temperatures[2]; for example the electrical resistivity, or the thermo-electric force of a cold-worked against an annealed metal[3]. It was thought to be an indication that stresses in the cold-worked material are at least mainly responsible for the broadening effect, since it seems plausible to assume that such stresses at any temperature cannot surpass the elastic limit (flow limit) of the material; the character of the stresses (length of the homogeneity region) determines the size of lattice region to which this quantity is related. As the elastic limit decreases with increasing temperature, the stresses which occur on heating will diminish rapidly to the value appropriate to that temperature, and will not alter very much more, or will alter only very slowly, on prolonged heating.

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IV. OTHER EFFECTS OF INTERNAL STRAINS

INTERNAL STRAINS AND MAGNETISM

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ABSTRACT. The magnetic properties from which a numerical value can be obtained for the internal stress σ_i are collected together, and the 180° walls are considered in detail. Their energy is determined theoretically and experimentally. They play a decisive role in the understanding of the coercive force.

The sciences of the mechanical and the magnetic properties of metals show a very remarkable similarity in their development. In each of them, there is one group of properties (*a*) which is susceptible of theoretically exact treatment by rigorous methods, while the theory of the other group (*b*) is vague and even in the most favourable cases only qualitative. Unfortunately it is the properties in the second group which are of particular interest in most practical cases and which lead to the typical differences between materials. In mechanics the density and elastic constants belong to the first group, in ferromagnetism the saturation intensity and the Curie temperature. In the second group (*b*) are the critical shear stress and the elastic yield point in mechanics, and the permeability and coercivity in magnetism. In both cases most of the substances with which we are concerned are somewhat similar as regards their properties in group (*a*), while those in group (*b*) can be altered several hundredfold by apparently small additions to the substance. The origin of this difference lies in the fact that we are concerned in the first case with a group of properties which concern the ideal lattice; in the second with one which depends on deviations from it, whether occurring naturally or produced by artificial means.

The fundamental task, then, is to describe the relevant deviation from the ideal lattice correctly. The words "internal strains" mean, in their widest sense, simply deviation from the ideal lattice. At present no really satisfactory description has been given. In each special case the most suitable model for describing the observed phenomena under discussion must be found. The pictures of internal strain which have been used to describe mechanical properties on the one hand and magnetic properties on the other are therefore very different. In the present state of research there seems only to be a slight connexion between the two kinds of internal strain, and we are still a long way from our aim of describing both sets of phenomena in terms of the same model, although it has long been known that there is a qualitative connexion between mechanical and magnetic hardness.

In this article we shall collect together all the evidence about internal strains that can be drawn from magnetic evidence. From among the huge number of parameters which would be included in a complete description, we shall actually

choose only a few. It is thus not surprising that different parameters are important for different phenomena. In the following we shall define the internal tension practically only through its mean value in a large volume, the mean value of its fluctuations and the order of magnitude of the regions in which a uniform strain may be assumed.

MAGNETIC METHODS FOR THE MEASUREMENT OF σ_i*

There is one point of departure common to all methods, and that is the dependence of the free energy F_σ on the direction of spontaneous magnetization I_s

$$F_\sigma = -\tfrac{3}{2}\lambda\sigma \cos^2\theta, \qquad \text{.....(1)}$$

where θ is the angle between the applied tension σ and the vector I_s. λ stands for the saturation value of the magnetostriction, which for simplicity we assume to be isotropic. Relation (1) is well founded thermodynamically and has been verified experimentally by measurements on nickel under stress. According to this relation, I_s is parallel to σ for positive magnetostriction, and perpendicular if λ is negative. In addition to (1) the direction of I_s is influenced by the crystal energy

$$F_K = K(\alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2 + \alpha_1^2\alpha_2^2), \qquad \text{.....(2)}$$

where α_i are the direction cosines of I_s with respect to the axes of the (cubic) lattice. For the real behaviour of a material the value of the quotient $\lambda\sigma/K$ is decisive. In the extreme case $\lambda\sigma \gg K$ the orientation of I_s is determined by the applied stresses, but if $\lambda\sigma \ll K$ it is determined by the crystal axes.

Formula (1) is experimentally verified if the stress is macroscopic. However, the essential generalization in all theories consists in the introduction of the internal stress σ_i. This quantity is assumed to vary from point to point in such a way that there is a preferential direction of I_s at every point, according to the law

$$F_{\sigma_i} = -\tfrac{3}{2}\lambda\sigma_i \cos^2\theta. \qquad \text{.....(3)}$$

We may attempt to give a more exact definition of σ_i in the following way: Let σ_{I}, σ_{II}, σ_{III} be the three principal stresses at a given point in descending order of magnitude, then σ_i has the direction of σ_{I} and has the magnitude

$$\sigma_i = \sigma_{\mathrm{I}} - \tfrac{1}{2}(\sigma_{\mathrm{II}} + \sigma_{\mathrm{III}}).$$

It is possible to verify equation (3) by studying the consequences of this assumption for various phenomena which are connected with the magnetization. If (3) is correct, it should be possible to describe all of them with the same assumptions as to σ_i. Among these phenomena the following may be mentioned.

THE INITIAL SUSCEPTIBILITY χ_a

In the case $\lambda\sigma_i \gg K$ the direction of I_s is determined everywhere by the direction of σ_i, and can be changed slightly by a weak magnetic field. For an isotropic distribution of σ_i it follows from this that

$$\chi_a = \tfrac{2}{9} I_s^2 / |\lambda|_{\sigma_i}, \qquad \text{.....(4)}$$

where σ_i stands for a conveniently defined mean value.

* R. Becker, *Phys. Z.* **33**, 905 (1932). A more exact treatment is contained in a book shortly to be published by R. Becker and W. Döring.

But even in the case $\lambda\sigma_i \ll K$ formula (4) is essentially correct. It is true that in this case I_s is practically parallel to the crystal axes when K is positive, but among these one is always preferred if σ_i is not zero. For example, a surface on which the stress in, say, the x-direction vanishes must separate two regions, in one of which the magnetization lies in the x-direction, and in the other is perpendicular to it. We speak in this case of a 90° wall between two regions which are homogeneously magnetized. A small magnetic field in the x-direction exerts a hydrostatic pressure on such a wall of which the magnitude is $H_x I_s$. Its effect is to extend the x-region at the expense of its neighbours (*Wandverschiebung*). This brings about an increase in magnetization which can be represented fairly well by equation (4).

It has been shown by Kersten[1] that there is a connexion between the quantity entering into (4) and the true strain. If a nickel wire is stretched plastically it becomes harder not only mechanically but also magnetically, i.e. χ_a decreases. Kersten found that in the case of plastically stretched nickel wire the quantity σ_i which determines χ_a according to (4) was about a quarter of the tension applied previously.

The reversible work of magnetization U should be given by equation (3). If a nickel wire whose internal stresses are isotropic and for which $\lambda\sigma_i \gg K$ is magnetized up to saturation, we should expect to find $U = |\lambda|\sigma_i$. Experiment[2] confirms the relation which is thus obtained between the initial permeability and the work of magnetization.

The quantity σ_i was defined originally with the help of χ_a through equation (4). It is very important to prove that it really stands for an internal stress. This is done by experiments which relate it to a stress σ which is simultaneously applied from the outside. Such a stress can of course have marked effects on the direction of I_s only if it is comparable with σ_i. In particular if $\sigma \ll \sigma_i$ we must expect effects which are proportional to the quotient σ/σ_i. Among these effects on σ/σ_i the following may be mentioned.

The displacement of the remanence I_R by external stresses. In the ideal case $\sigma_i = 0$, the application of a simple pull should make I_R either equal to zero or to I_s according to the sign of λ. In reality a law of the form

$$(dI_R/d\sigma)_{\sigma \to 0} = \tfrac{1}{4} I_s/\sigma_i$$

is found. This yields another method for the determination of σ_i.

THE ΔE EFFECT

A ferromagnetic under tension which is not magnetized as a whole increases its length for two reasons. One is a purely elastic extension σ/E_0, but to it we must add a second extension which is due to the fact that the distribution of the various directions of I_s is changed through the presence of σ; this change, in turn, gives rise to an additional extension, because of the magnetostriction associated with it. This effect too must obviously be proportional to σ/σ_i as well as to the constant of magnetostriction $|\lambda|$. As a result the extension ϵ is increased and Young's modulus E diminished:

$$\epsilon = \sigma/E = \sigma/E_0 + C\,|\lambda|\,\sigma/\sigma_i.$$

For a hard material the exact calculation gives to C a value of about $\frac{2}{5}$. This effect is accessible to observation because we observe the expansion σ/E_0 alone if we carry out our measurements in the presence of a strong magnetic field. The difference between E_0 (with magnetic field) and E (without magnetic field) thus provides another possible method of measurement of σ_i.

All these methods have given the same value of σ_i within the accuracy which could reasonably be expected. We may say as a consequence that this "magnetic" internal stress is a useful quantity to characterize the deviations from the ideal lattice structure.

All these methods fail to give much insight into the true nature of the internal stresses. Our knowledge can be extended, however, through the following considerations on 180° walls. They enable us to determine the mean length l within which tensions may be taken as homogeneous.

THE 180° WALLS

We call a surface a 180° wall if it separates two regions of antiparallel I_s. Such walls and their displacements form a case apart, because, according to the stress theory developed above, they should be unstable. According to this theory they would vanish if subjected to an arbitrarily small magnetic field. For both the elastic energy F_σ and the crystal energy F_K are invariant with respect to a reversal of the direction of I_s. Experimentally, these 180° walls make their appearance in the well-known investigations of Sixtus and Tonks[3] on iron-nickel wires under stress. In these experiments the axis of the wire is so strongly a preferential direction for I_s that the hysteresis curve becomes rectangular; the change of magnetization thus takes place in a single Barkhausen jump of magnitude $2I_s$ which runs through the wire.

This experiment, while demonstrating a 180° wall in motion, shows us that this motion requires a certain minimum field strength H_0. We may assume that in a material with irregular internal stresses the coercive force H_c is of a similar origin to the critical field strength H_0 of Sixtus and Tonks.

The basis for a theory of this phenomenon has been developed by Bloch[4]. He was the first to point out that the wall itself has a finite thickness δ and a finite energy γ. Either quantity depends essentially on the state of stress. For an irregular distribution of internal stresses the surface energy thus becomes a function of the location. The wall prefers those locations for which γ is a minimum. It needs a finite field to drag it over places where γ is a maximum. If we consider only displacements in one coordinate direction, we find for the critical field the condition

$$2H_0I_s=(\partial\gamma/\partial x)_{\max}. \qquad \ldots\ldots(5)$$

For $2H_0I_s$ is the pressure on the wall due to the field, while $\partial\gamma/\partial x$ is the opposing force due to the tensions. The analysis of the idea contained in (5) will give us further knowledge of the structure of the internal stress field. As a start we shall have to find formulae for the thickness of the wall δ and its specific energy γ.

The computation of γ and δ was carried out in principle by F. Bloch[4] in 1932. We can get a simple estimate from the following considerations: It is easy to see that the transition from one direction of magnetization to the opposite one cannot be completely abrupt, for the electron spins are coupled by the exchange interaction which tends to make them parallel to each other. As a consequence, an abrupt change of direction of the spins at the wall is ruled out by energy considerations. If the exchange were the only force acting on the spins it would make the transition as smooth as possible; this would bring about a very thick region of transition.

The external tension applied, however, acts in the opposite sense, namely it tends to make the wall as thin as possible; for the thicker the wall the more spins are at an angle to the preferred direction of magnetization which is determined by the external stress. As a result of the competition between exchange and tension we get a medium thickness of the region of transition such that the sum of the two contributions to the energy of the wall becomes a minimum.

We can easily find δ and γ from these considerations. Taking the Heisenberg model of ferromagnetism as a basis, we associate one electron spin with each atom and the exchange interaction is only taken into account between neighbours. In addition, we limit ourselves to a cubic lattice and neglect the crystal energy in comparison with the elastic energy. Before carrying out a more exact calculation let us estimate the order of magnitude of δ and γ to within a factor of the order of unity. Let the z-axis be the preferential direction; the wall is to be parallel to the yz plane so that the direction of the spin depends only on the x-coordinate.

As an abbreviation we denote by $C = 3\lambda\sigma/2$ the energy required to turn the magnetization from its preferred direction into an orientation perpendicular to the latter. The contribution of the elastic energy to the energy of the wall is then $C\delta$, within a factor of the order unity, for in making 1 cm^2 of the region of transition we have to turn the magnetization out of its preferred direction throughout a volume δ. The contribution of the elastic term to the energy of the wall is thus smaller, the more sudden the transition. Further energy is required to twist two spins out of a parallel position into one where there is an angle ϵ between them. From the quantum theory we find its value to be $\frac{1}{2}I(1-\cos\epsilon)$, where I is the exchange integral. Since in our case the angles between neighbouring spins are small, we may take $\frac{1}{4}I\epsilon^2$ as an approximation. Because of our simplifying assumptions about the position of the wall, the angle ϵ is different from zero only for pairs with different x-coordinates.

Along the length δ the angular deviation from the direction of preference must increase from 0 to π. If a is the lattice parameter, this increase takes place in steps of δ/a; it follows that the mean angle between two neighbouring spins is $\pi a/\delta$. The number of spins having neighbours in the x-direction is δ/a^3 for 1 cm^2 of the wall. Hence neglecting a numerical constant, the contribution of the exchange energy to the energy of the wall is

$$I(a/\delta)^2\,\delta/a^3 = I/\delta a.$$

This quantity decreases with increasing δ, i.e. it is smaller the smoother the transition. We now get for the total energy of the wall

$$\gamma = C\delta + I/a\delta.$$

The actual thickness is such that γ is a minimum. By differentiation it follows that

$$\delta \simeq (I/aC)^{\frac{1}{2}}. \qquad \text{.....(6)}$$

Introducing instead of I the exchange energy per cm^3, $A = I/a^3$, we get

$$\delta/a \simeq (A/C)^{\frac{1}{2}}.$$

Thus if we measure the thickness of the region of transition in terms of the lattice parameter it is about equal to the square root of the ratio between exchange and elastic energies. These energies are approximately in the same ratio as the internal field and the field which is necessary to produce saturation in a direction perpendicular to the stress. In normal cases this ratio is about 1000 or 10,000. Correspondingly we find for δ values between 30 and 100 lattice-distances. For the energy of the wall we find from the values of δ just obtained

$$\gamma \simeq 2\,(IC/a)^{\frac{1}{2}} = 2a\sqrt{(AC)} = 2I/a^2\, a/\delta. \qquad \text{.....(7)}$$

From the last form it can very clearly be seen that this value of γ is very much smaller than it would be for an abrupt transition. If the direction of the spin changed suddenly from one preferential direction to the other, the energy per unit area required would be I/a^2. The value obtained above is smaller than this by the factor $2a/\delta$. Since we can obtain an approximate value for I from the Curie temperature, γ can be calculated without any difficulty. In normal cases values ranging from 1 to 3 ergs/cm^2, i.e. somewhat smaller values than for the surface energy of ordinary liquids, are obtained.

The calculation can be carried out without difficulty with more rigour and generality. It is found that the formula

$$\gamma = 2a\sqrt{(AC)} \qquad \text{.....(8)}$$

is also correct for the body-centred and face-centred cubic lattices if A always represents the exchange energy per cm^3.

The measurement of the energy of the wall has been made possible by an analysis of the nuclei of magnetization as obtained by Sixtus[5] (figure 1). He worked on wires for which the axis was a preferential direction of magnetization. Let us assume it to be magnetized first towards the left (by a field due to the coil Sp_0). Then a main field H towards the right is produced by this coil. This field is slightly larger than H_0 but it is not sufficient for the production of a nucleus of magnetization which points to the right. The change of magnetization sets in only if a strong additional field is switched on with the help of a short coil Sp_1. Thus a nucleus is produced which, by growing in the main field, changes the magnetization of the entire wire. Sixtus found that whenever the field within the coil Sp_1 exceeded the starting field, a nucleus was created. Yet if the additional field was switched off very quickly, the nucleus immediately stopped growing. Such nuclei are conserved

unaltered within the wire for any length of time. One can easily determine their magnetic field and thus get an idea of their magnitude. It is found that they are always very long and thin. Sixtus found that the length had values up to 13 cm. while the diameter was below 0·1 mm., that is, about one-third of the diameter of the wire. It is surprising in that connexion that the length was very much greater than the length of the starting coil, which was only 1 cm. The ends of the nucleus have thus grown out of the additional field into a region where its direct effect can no longer be felt.

Next we must discuss the question why the large frozen-in nuclei cannot grow in the main field. This is ultimately due to the interaction between the surface energy and the demagnetizing field which is formed in the neighbourhood of the nucleus. In the interior of the nucleus and at its sides the demagnetizing field due to the free poles at the surface of the nucleus is in the opposite direction to the external field. Owing to this any movement of the boundary on the sides of the nucleus is prevented, so that it cannot get any thicker. At the ends, on the other

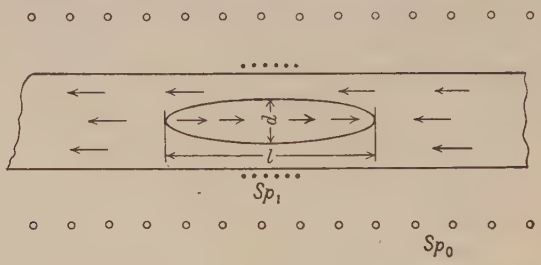


Figure 1. A nucleus of magnetization, magnetized to the right, of length l and thickness d in a wire which is saturated to the left outside. Sp_0 and Sp_1 are the coils which produce the main field and the starting field.

hand, growth is prevented because the spreading of the wall there would lead to a large increase in the surface. We may say that, because of the large curvature at the ends, there is a pressure on the interior of the nucleus. The wall can only be shifted if the pressure due to the field, $p = 2HI_s$, is greater than the pressure due to the surface tension of the boundary. As the external field is increased, growth begins at a definite field strength H_s' which depends on the size of nuclei and naturally is always smaller than H_s.

For a more exact treatment we consider the conditions which the energy must fulfil to enable the nucleus to shift its boundary in such a way that its volume increases. Consider a long thin nucleus of volume V. We assume the nucleus to be symmetrical about an axis parallel to the axis of the wire. Deviations from this shape should never be large for long nuclei. In special calculations, later on, we shall treat the nucleus as an ellipsoid of revolution. We call l the length of the nucleus and d the largest diameter. We assume $l \gg d$. The ratio l/d was always greater than 500 for the nuclei found by Sixtus.

The magnetic field adds an energy $2HI_s dV$ to the energy of the metal, when the nucleus, moving its boundary, increases its volume by dV, as the magnetization in that volume, first opposed to the direction of the field, becomes parallel to that

direction. This energy is used in several ways. First of all, the shift of boundary is connected with an increase of surface dO for which a surface energy $\gamma\, dO$ is needed. Moreover, a change will occur in the energy of the demagnetizing field. Let W be this field energy and dW its variation. We write

$$dU = 2HI_s dV - \gamma\, dO - dW \qquad \text{.....(9)}$$

for the difference between the energy $2HI_s dV$ gained, and the sum of the energies expended in this process. If the spreading of the wall were possible without energy loss, the nuclei could start growing as soon as the energy gained, $2HI_s dV$, exceeded $\gamma\, dO + dW$, the energy being utilized, in fact, as soon as dU was positive for a positive dV. The existence of the limiting field H_0, however, shows that even for a very slow shift of the boundary, an amount of energy $2H_0 I_s$ is spent irreversibly for every cm^3 swept out by this boundary. Because of this friction, the nucleus will only grow when

$$dU > 2H_0 I_s dV, \qquad \text{.....(10)}$$

in other words, when dU is greater than the energy lost through friction in the shifting of the wall.

There are only two essentially different growth processes for a long thin nucleus, namely growth of the length l or of the thickness d. l and d could of course also grow simultaneously, but this could only happen if the inequality (10) were satisfied at the same time for growth in length at constant thickness, and for growth in thickness at constant length, as the shift in boundary occurs at totally different places for the two processes—at the ends in the one case and on the sides in the other. We may therefore consider the two processes of growth as independent of one another. For a very long thin nucleus we have

$$V = C_1 l d^2 \quad \text{and} \quad O = C_2 l d,$$

where

$$C_1 = \pi/6 \quad \text{and} \quad C_2 = \pi^2/4.$$

If the nuclei which we consider are long enough, we may drop the energy W of the demagnetizing field. The quantity U, of which (9) gives the differential, may then be written

$$U = 2C_1 HI_s l d^2 - C_2 \gamma l d. \qquad \text{.....(11)}$$

Growth in length will be possible if $\partial U/\partial l > 2H_0 I_s\, \partial V/\partial l$. Substituting in this condition the approximate expression (11) for U, it yields

$$d > \gamma C_2 / 2I_s (H - H_0) C_1. \qquad \text{.....(12)}$$

Growth in length will therefore be possible only if the thickness d exceeds a certain critical thickness $d_K = \gamma C_2 / 2I_s (H - H_0) C_1$. Growth in length is inhibited for thinner nuclei. d_K is inversely proportional to the effective field strength $(H - H_0)$:

$$d_K = \beta/(H - H_0),$$

where β is the critical thickness for a field unity. For an ellipsoid of revolution we have $\beta = 3\pi\gamma/4I_s$. We find in a similar way the condition for growth in thickness

$$\frac{\partial U}{\partial d} > 2H_0 I_s\, \partial V/\partial d,$$

from which follows, neglecting W, $d > \frac{1}{2}d_K$. Growth in thickness is therefore possible when the thickness exceeds $\frac{1}{2}d_K$. Growth in thickness will start before growth in length for long thick nuclei, because the volume increases quadratically with thickness but only linearly with length. The increase in volume will thus be greater for growth in thickness than for growth in length, when the surface grows by the same percentage in the two cases. The thickness below which the growth in thickness is inhibited increases when the ratio of the dimensions l/d decreases. If this ratio becomes so small that the demagnetizing field H_d on the side of the nucleus becomes equal to the difference of field strength $(H - H_0)$, then the total effective field at these points is equal to zero. No growth in thickness will then be possible for any nucleus.

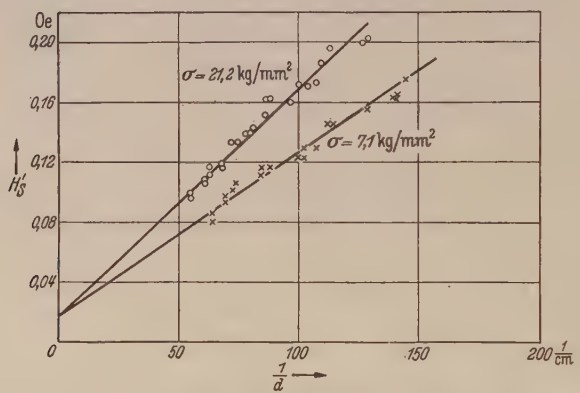


Figure 2. The magnitude H_s' of the main field necessary to start a nucleus, as a function of the reciprocal thickness $1/d$ of the nucleus. Two different values of the applied tension are shown.

The situation is different for growth in length. The demagnetizing field does not inhibit the growth at the ends, but furthers it, as the field energy W decreases for increasing length and constant thickness. The thickness above which growth in length is allowed by energy considerations will therefore drop from d_K to lower values, when the ratio of dimensions l/d decreases.

The corresponding calculation was made by W. Döring[6]. He reached the conclusion that the thickness of the nucleus which can grow under the influence of a field H is somewhat smaller than the value given by (12), namely five-sixths of this value. Therefore

$$d_0 = \frac{5\pi\gamma}{8I_s(H - H_0)}.$$

Conversely, this formula gives us the field strength H_s' required to start the wave from a nucleus of thickness d

$$H_s' = H_0 + 5\pi\gamma/8dI_s. \qquad \ldots\ldots(13)$$

This relation between H_s' and d has been examined by H. Haake[7] for five different values of the external tension for the same wire. Two series of these measurements are represented in figure 2. The values of the surface energy computed from these data are given in figure 3 as a function of the external tension.

The vertical intervals marked on the figure indicate a 10 per cent range of error. These values must now be compared with formula (8). The exchange integral I can be derived from the Curie temperature. According to Heisenberg we have for a face-centred cubic lattice

$$k\theta = \frac{2I}{1-\sqrt{3}/3} = 4{\cdot}73I.$$

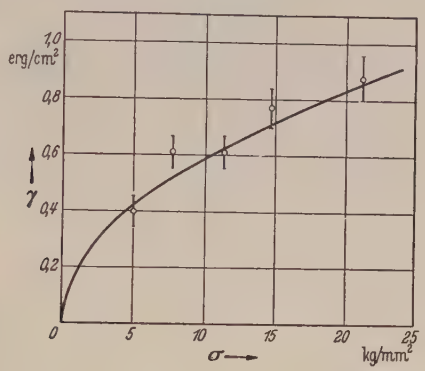


Figure 3. The specific energy γ of the wall as a function of the applied tension σ. Theoretical dependence given by (14), ϕ measured values, taken from the slope of the straight lines in figure 2.

Using the relation $A = 4I/a^3$, we therefore find for the specific surface energy

$$\gamma = 2{\cdot}26\,(k\theta\sigma\lambda/a)^{\frac{1}{2}}.$$

Using the figures $\theta = 850°$ K., $\lambda = 2\times10^{-5}$, $a = 3{\cdot}59$ A., we find

$$\gamma = 0{\cdot}185\,\sigma^{\frac{1}{2}} \text{ erg/cm}^2 \quad (\sigma \text{ in kg./mm}^2). \qquad \ldots\ldots(14)$$

This curve is drawn in figure 3. We see that the agreement between the theoretical formula and the experimental data is surprisingly good. Considering the crude assumptions on which the theoretical calculations are based, one could hardly have expected so good an agreement. Bloch himself only considered his formula as an estimate which might easily be half or twice the true value. In the present case a factor of 2 would completely spoil the agreement with experiment.

THE LIMITING FIELD STRENGTH H_0

According to the ideas developed above, this quantity is essentially determined by the relation

$$2H_0I_s = (\partial\gamma/\partial x)_{\max}.$$

The dependence of γ on x is essentially determined by the dependence of σ on x. For this dependence of σ on x we must clearly distinguish between two different cases. The question is whether the wave-length of the internal stress is large or small compared with the thickness of the wall. Both cases are represented schematically in figure 4. The stress fluctuation is represented there by a stress hump of

height $\Delta\sigma$ and width l. In the first case $\delta \ll l$, in the second case $l \ll \delta$. We may regard σ as constant throughout the wall in the first case, and we find therefore

$$\frac{\partial \gamma}{\partial x} = a\sqrt{\left(\frac{A}{C}\right)}\frac{\partial C}{\partial x}.$$

As $\delta = a\sqrt{(A/C)}$ and $C = 3\lambda\sigma/2$, this formula becomes

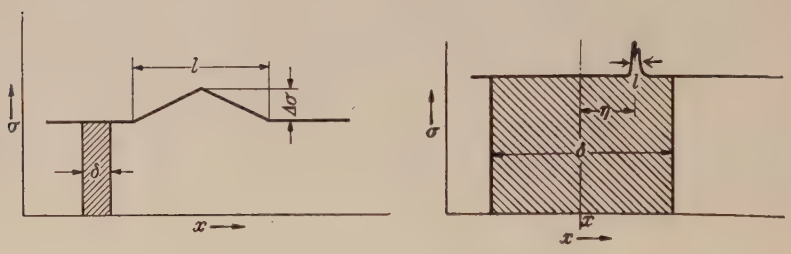
$$\frac{\partial \gamma}{\partial x} = \tfrac{3}{2}\lambda\delta\frac{\partial \sigma}{\partial x}.$$

For our stress hump we find $\partial\sigma/\partial x = 2\Delta\sigma/l$ and therefore

$$\frac{\partial \gamma}{\partial x} = 3\lambda\Delta\sigma\frac{\delta}{l},$$

and

$$H_0 = \frac{3}{2}\frac{\lambda\Delta\sigma}{I_s}\frac{\delta}{l} \quad (\delta \ll l). \qquad \ldots\ldots(15a)$$



a *b*

Figure 4. Schematic picture of the two limiting cases $\delta \ll l$ (4*a*) and $\delta \gg l$ (4*b*).

In the second case we have a sharp stress concentration, and the increase $\Delta\gamma$ of surface energy is equal to the stress energy added at this point. Therefore

$$\Delta\gamma = \tfrac{3}{2}\lambda \sin^2\theta \int(\sigma - \sigma_0)\, dx,$$

which gives in our special case

$$\Delta\gamma = \tfrac{3}{2}\lambda \sin^2\theta\ \tfrac{1}{2}l\Delta\sigma,$$

and

$$\frac{\partial \gamma}{\partial x} = \tfrac{3}{4}\lambda l\Delta\sigma . 2 \sin\theta\cos\theta\frac{\partial \theta}{\partial x}.$$

Inside the wall we have $\partial\theta/\partial x \simeq \pi/\delta$. A precise calculation gives

$$(\partial\gamma/\partial x)_{\max} = 1{\cdot}15\lambda\Delta\sigma\ l/\delta,$$

and hence

$$H_0 = 0{\cdot}58\frac{\lambda\Delta\sigma}{I_s}\frac{l}{\delta} \quad (l \ll \delta). \qquad \ldots\ldots(15b)$$

The dependence of H_0 on l/δ is represented in its main features by figure 5. H_0 has a maximum when l is approximately equal to δ, and decreases for higher values of l as well as for lower values. The maximum value is, within a factor which differs but slightly from unity,

$$H_{0\max} \simeq \lambda\Delta\sigma/I_s.$$

It is not worth while to compute the exact variation of H_0 in the neighbourhood of the maximum. Figure 5 is only approximate in this respect. We should not give too much weight to the quantitative results of our calculations, as our assumptions about the stress distribution are only schematic. These results should, however, be correct in a qualitative way for the actual distribution of disturbances. In this way we connect H_0 with the stress fluctuation $\Delta\sigma$ by a formula of the form

$$H_0 = p_0 (\lambda \Delta\sigma / I_s), \qquad \ldots\ldots(16)$$

where p_0 is a numerical factor dependent on the distribution of internal stresses in space. p_0 reaches its maximum value, approximately unity, when the "wavelength" of the stress fluctuations is almost equal to the wall thickness. When $l \ll \delta$ the order of magnitude of p is given by $p \simeq l/\delta$. For $l \gg \delta$ we have approximately $p \simeq \delta/l$.

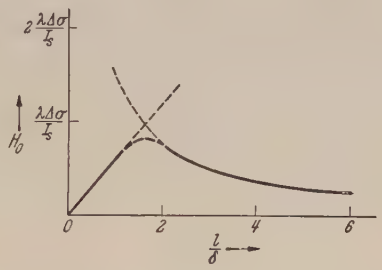


Figure 5. The limiting field strength H_0 as a function of l/δ for stress humps with the same $\Delta\sigma$.

Measurements of the initial permeability of the same wire without external tension would allow a rough check on this equation of the limiting field strength. We may well assume that the stress fluctuations $\Delta\sigma$ then remain as internal stresses σ_i. The only available data for this comparison with theory are given in a series of measurements by Preisach[8] in which, from the experimental values of H_0 (with σ) and χ_a (without σ), values of p_0 from 0·1 to 0·4 may be calculated.

THE COERCIVE FORCE*

It is obvious that we can make use of these considerations about H_0 to develop a qualitative theory for H_c. We may imagine that H_c has the task of driving the 180° walls through certain isolated spots in spite of the fact that the material is isotropic as a whole. There are, however, some essential differences. We had assumed above that the stress σ was only subject to small relative fluctuations around a certain mean value. We could therefore assume the thickness δ to be approximately constant. Now this is no longer true. In an ordinary material the stress oscillates between zero and an upper limit. Hence δ itself varies from place to place in a very irregular manner. However, qualitatively there will still exist a

* Cf. in particular M. Kersten, in *Probleme der Technischen Magnetisierungskurve*, edited by R. Becker (Berlin, 1938).

relation for H_0 very similar to (16). We have only to replace the fluctuation of the stress $\Delta\sigma$ by a mean value of the internal stress itself, i.e.

$$H_0 = p_0 \lambda \sigma_i / I_s .$$

The magnitude of the factor p_0 which depends on the internal stress distribution can no longer be ignored. Even now it is still true that p is small if the disturbances are highly localized or very smooth; it will again have a maximum value of the order unity if the internal stress fluctuates between its extremes within a medium length; but it is difficult to say what this critical stress distribution with maximum p will look like.

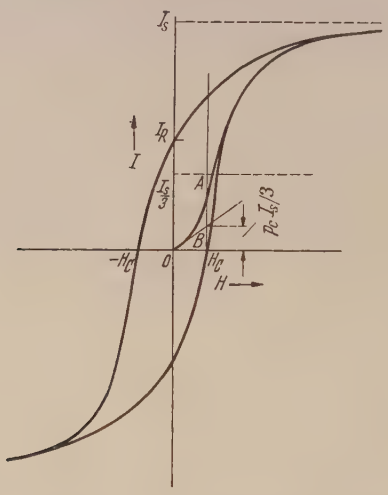


Figure 6. The initial susceptibility related to the coercive force through the number p_c.

Because of this theoretical uncertainty in the determination of H_0 it is not worth while to consider how the total coercive force H_c is connected with the value of H_0 in various regions. H_c must be somewhat larger than the mean value of H_0; for we had always assumed in estimating the latter that the field strength was parallel to the preferential direction. Now the field strength necessary to change the direction of magnetization will be larger, if it forms an angle with the preferred orientation, because only the component of the field parallel to this direction will be active in exerting a pressure on the wall. If we take this effect of the orientation of the regions into account, we find a factor of about $\frac{3}{2}$. Hence we put for the total coercive force

$$H_c = \tfrac{3}{2} p_c \lambda \sigma_i / I_s ,$$

where p_c is a factor of the same nature as p_0. If we make use of equation (4) and express σ_i in terms of the initial permeability χ_a, we get

$$H_c = \tfrac{1}{3} p_c I_s / \chi_a . \qquad \text{.....(17)}$$

We can use this relation to determine p_c experimentally. The significance of this quantity can be seen from figure 6. If we construct a parallel to the I axis at

the point $H = H_c$, the initial tangent to the original curve intersects it at the height $p_c I_s/3$.

If we make use of the fact that the number p_c has a maximum of the order unity, we can reach an important estimate for the maximum value of the coercive force compatible with a given σ_i. We get

$$H_{c\max} \simeq \tfrac{3}{2}\lambda\sigma_i/I_s.$$

This formula reproduces well the order of magnitude of the biggest values of H_c obtained so far. With $\sigma_i \simeq 500$ kg. mm$^2 = 5 \times 10^{10}$ dyne cm^2, $I_s = 1500$ and $\lambda = 10^{-5}$, we get, for instance, $H_c = 500$ Oersted, which is certainly of the right order of magnitude. The smallest values are reproduced correctly too in their order of magnitude if we put $\sigma_i \simeq \lambda E$, which amounts to the assumption that there are no stresses in the material except for the inevitable stresses due to magnetostriction.

The previous considerations on the coercive force yield, therefore, in addition to the quantity σ_i (the gross value of the internal stress), another number p_c, which depends on the ratio between the thickness of the wall and the wave-length of the internal stresses. The experimental material is not yet available, yet this approach to the structure of the field of internal stresses is a fruitful one. It would be specially helpful in this connexion to relate the magnetic values of σ_i and p with those numbers which can be deduced from the study of the mechanical strength of materials.

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INTERNAL FRICTION IN SOLIDS

By CLARENCE ZENER, College of the City of New York

ABSTRACT. The various causes of internal friction in solids are discussed. Internal friction depends in general on thermal currents which occur owing both to the inhomogeneous strains set up by the vibrations in the solid, and to the variations in the elastic constants from point to point in polycrystalline materials. The influence of ferromagnetism also is considered.

§ 1. INTRODUCTION

The term "internal friction" refers to the capacity of a solid to convert its mechanical energy of vibration into internal energy. This unavoidable degradation of energy manifests itself in many ways. It causes the gradual damping of a vibrating solid even when the solid is so supported as to transfer none of its energy to the surroundings. When such a solid is subjected to a periodic force, this continual change of ordered energy into disordered energy prevents the amplitude of vibration from becoming infinite when the frequency of the applied force approaches a natural frequency of the specimen. Finally, when a solid is coupled electromagnetically to an electrical circuit, it contributes not only to the inductance of the circuit, but also to its resistance.

These various manifestations of internal friction give directly various measures of internal friction. Thus observation of the rate of decay of free vibration gives directly the logarithmic decrement δ. Again, one obtains a second measure from a plot of the amplitude of vibration against frequency of exciting force near a resonance frequency. This is the ratio of the width of this resonance curve at half maximum, $\Delta\nu$, to the frequency at resonance ν. Finally, from the effective resistance R and effective inductance L of the solid coupled electromagnetically to an electrical circuit, one may form a third dimensionless quantity, $2\pi\nu(L/R)$. This ratio is called by electrical engineers the Q of the element. Measures of internal friction have also been used which are obtained from theoretical considerations. If ΔE is the energy dissipated per cycle, and E is the average energy of vibration during the cycle, the ratio $\Delta E/E$ gives a measure of the damping capacity of the solid. This measure is called the specific energy loss. Again, the phenomenon of internal friction may be treated phenomenologically in the theory of elasticity by regarding the elastic modulus as complex. The ratio of the real part of the modulus to the imaginary part is equal to the ratio already denoted by Q. The relation between these various measures is as follows

$$1/Q=\Delta E/2\pi E=\Delta\nu/\sqrt{3}\nu=\delta/\pi. \qquad \text{.....(1)}$$

No one of these is used universally. As his measure of internal friction the writer has adopted $1/Q$.

The measured internal friction includes both the energy dissipated by the specimen and also that dissipated to the surroundings. While acoustical losses are

readily eliminated, loss of energy through the supports is especially elusive. Unfortunately many experiments during this century have not profited from the early work of Voigt[1], which showed the extreme care which must be taken to avoid such losses when the internal dissipation is small. A convenient method of avoiding these losses, the one used in this laboratory, is shown in figure 1. The specimen is supported by silk threads at its nodes of vibration. The driving force is obtained by the reaction upon a permanent magnet M of the eddy currents induced by an alternating current in the driving coil. An alternating electromotive force is induced in a detector coil at the other end by the eddy currents arising from the motion of the specimen in the field of a second permanent magnet M'.

The internal friction of solids covers a wide range. Q varies from near unity for highly damped solids to more than 1,000,000 for quartz[2,3]. The value of Q for dry wood[4] is of the order of 100. Metals cover a wide range, with values of Q

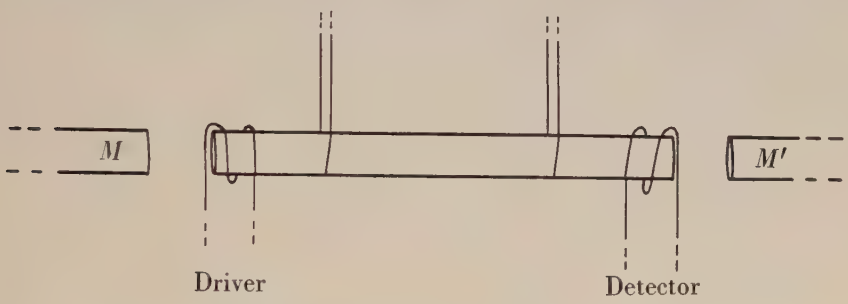

Figure 1. Method of measuring internal friction for strains less than 10^{-5}; after Randall, Rose and Zener[16].

ranging from less than 100 to more[16] than 200,000. The internal friction of metals is particularly interesting since for any particular metal it varies widely according to the conditions of measurement and to the past history of the specimen.

The internal friction of metals is independent of the amplitude of vibration used in its measurement only if this amplitude is extremely small (strain less than 10^{-5}). A typical example of variation with amplitude is seen in figure 2. In order to avoid this variation the amplitude must be so small that optical methods of detection are too insensitive. Fortunately the modern technique of electrical amplification enables one to measure[5] the internal friction even when the maximum strain is as low as 10^{-8}. According to Föppl[6] internal friction of large amplitude is primarily a measure of the capacity of a metal to undergo plastic flow under large stresses. It is hence incapable of yielding information concerning metals not previously disturbed by plastic flow. For this reason this paper is devoted exclusively to internal friction measured with small amplitudes of vibration (maximum strain less than 10^{-5}).

The internal friction of a metal is generally a function of the frequency of measurement[1,5], while that of dielectrics appears to be independent of this frequency[4,7]. Gemant[8] has developed a theory of the internal friction of solid dielectrics which interprets this independence of frequency.

The internal friction of a metal increases in a characteristic manner with the temperature of measurement[9, 10, 11]. The type of variation obtained is shown in figure 3. Förster and Köster[10] have attributed this rapid rise with increasing temperature to the onset of slip at high temperatures.

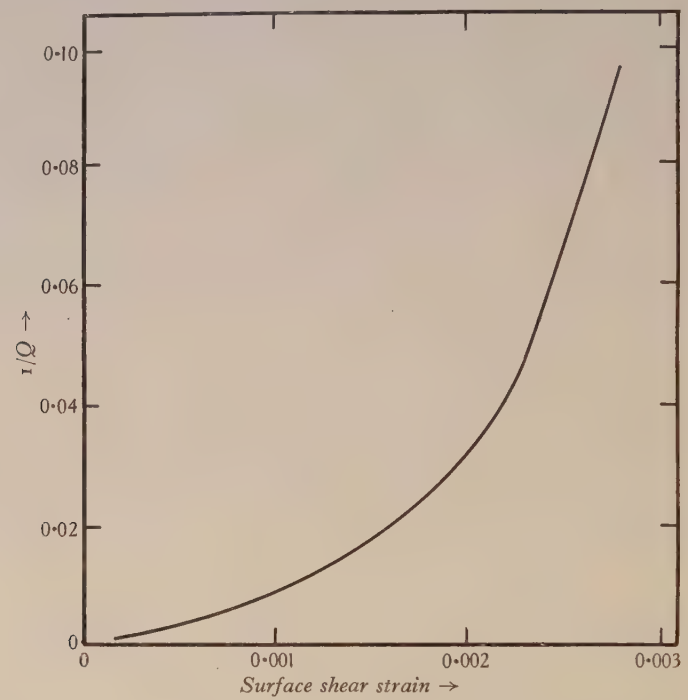

Figure 2. Dependence of internal friction upon amplitude of vibration. Example of torsional vibration of nickel-steel bar, after Föppl[6].

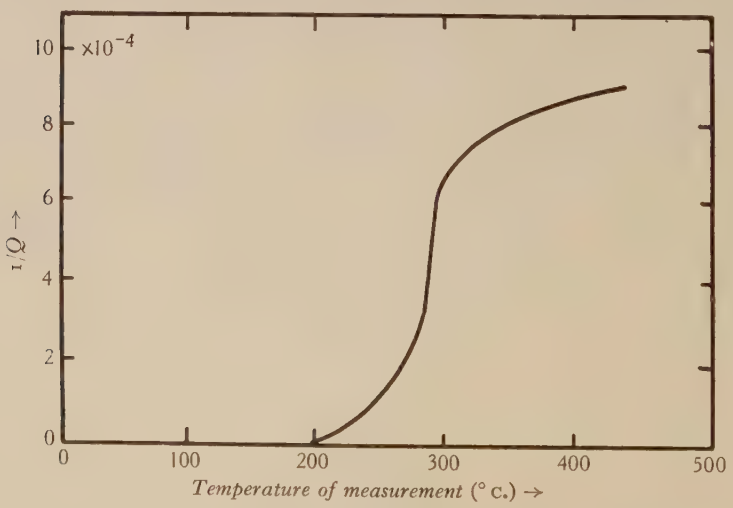

Figure 3. Dependence of internal friction upon temperature of measurement. Example of magnesium, after Förster and Köster[10].

The internal friction of metals is affected more than any other property by the past history of the specimen. A striking example is the variation of the internal friction with the annealing temperature of a previously cold-worked specimen[5, 10, 11]. Figure 4 shows the type of variation found. The damping has been decreased by a factor as large as 30 by annealing to just below the recrystallization temperature. This effect has been interpreted as due to the relief of internal stresses by low-temperature annealing. On the other hand, such annealing has no noticeable effect on the hardness of the specimen, and increases the elastic moduli by at most 5 per cent. The rapid rise upon annealing above the recrystallization temperature has been interpreted as due to an increase in grain size.

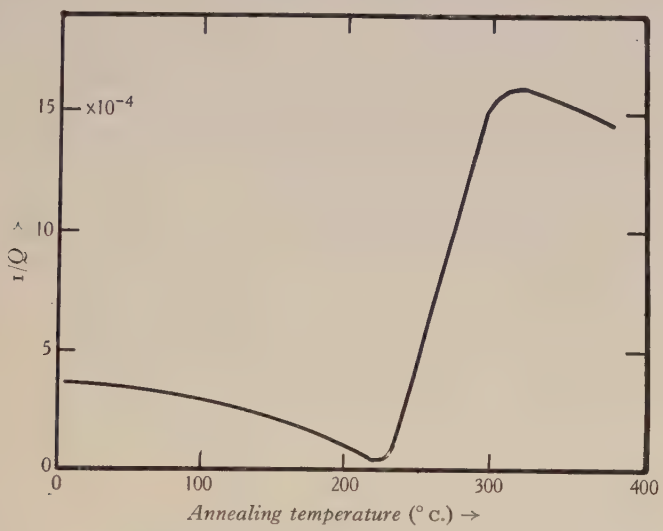

Figure 4. Dependence of internal friction upon annealing temperature. Example of copper, after Wegel and Walther[5].

§ 2. THERMAL CURRENTS AS A SOURCE OF INTERNAL FRICTION

A. *General theory*

We have seen that internal friction is an extremely structure-sensitive property. If all the causes of internal friction were thoroughly understood, we could use it as a powerful metallurgical tool. The realization of this potential importance of internal friction has furnished the incentive for the theoretical and experimental work reviewed in this section[12–16].

From the energetic standpoint, internal friction is simply the transformation of mechanical energy into internal energy. In searching for the causes of this transformation, it is natural to examine first the effects of the direct coupling between the mechanical and the internal coordinates of a solid. This is called the thermoelastic coupling. Its effects are seen in the cooling of a solid during an adiabatic expansion, and conversely, in the expansion of a solid heated under constant pressure. This thermoelastic coupling is operative only when the stresses in the

vibrating solid are inhomogeneous. Periodic changes in stresses during vibration give rise to periodic changes in temperature. If the stresses are not uniform, the temperature will likewise not be uniform. Gradients in temperature give rise to heat currents. But heat currents are necessarily associated with an increase in the entropy of the system. If the entropy of a freely vibrating solid is increasing, its internal energy must be increasing at the expense of its mechanical energy. Hence the thermoelastic coupling endows the solid with internal friction.

An insight into the factors which influence this thermoelastic internal friction may be obtained by considering the flow of heat to and from an idealized region in a specimen undergoing forced vibration. The region will be considered to have such a high thermal conductivity that it is at a uniform temperature. If the region were thermally insulated, its temperature would undergo periodic fluctuations. We shall denote by ΔT the amplitude of this temperature fluctuation. Since there is no flow of heat, the entropy remains unaltered. On the other hand, if it were connected by a perfect thermal conductor to a heat reservoir, vibration would be accompanied by a flow of heat back and forth between the region and the reservoir. We shall denote by $\Delta\mathcal{Q}$ the quantity of heat which thus flows back and forth. Again the entropy remains unaltered, since the flow of heat is between regions with the same temperature. We finally consider the region connected to the heat reservoir by a wall with a finite thermal conductivity. Such a wall introduces a finite time of relaxation τ for the establishment of temperature equilibrium. Thus in the absence of vibration, any temperature difference between our idealized region and the heat reservoir would decay exponentially as $\exp(-t/\tau)$. The now irreversible flow of heat across the temperature gradient of the wall results in a steady increase of entropy. An elementary calculation gives the entropy increase per cycle as

$$\Delta S = \pi T^{-2}\,\Delta T \Delta\mathcal{Q}\,\frac{\nu_0\nu}{\nu_0^2+\nu^2}. \qquad \text{.....(2)}$$

Here ν is the frequency of vibration, and $\nu_0 = 1/(2\pi\tau)$.

This expression for ΔS may be readily interpreted after rewriting it as the product of the two factors $2\Delta\mathcal{Q}\ \Delta T/T^2$ and $(\pi/2)\ \nu_0\nu/(\nu_0^2+\nu^2)$. The first factor is just the entropy increase which would accompany the flow of heat $\Delta\mathcal{Q}$ from the temperature $T+\Delta T$ to the slightly lower temperature T, and then back again to the still lower temperature $T-\Delta T$. The second factor takes account of the fact that the actual flow of heat is always less than $\Delta\mathcal{Q}$, and that the actual difference of temperature between region and heat reservoir is always less than ΔT. When $\nu \gg \nu_0$, the flow of heat is much less than $\Delta\mathcal{Q}$, and the vibration is nearly adiabatic. When $\nu \ll \nu_0$, the maximum difference in temperature is much less than ΔT, the vibration is nearly isothermal. These two regions are illustrated in figure 5.

The calculation of the entropy increase arising from thermal currents in an actual solid follows closely that for the above idealized system. We now denote by $\Delta T\,(x, y, z)$ the temperature change in the solid which would result if the vibration proceeded from zero to maximum strain adiabatically, and by $\Delta\mathcal{Q}\,(x, y, z)\,dv$ the corresponding heat flow from an element of volume dv if the vibration proceeded

isothermally. The relaxation of any temperature fluctuation in an actual solid may be described in the standard way by an expansion in terms of a suitable infinite set of eigenfunctions. Each such function is associated with a definite time of relaxation. A calculation[13] similar to that for the idealized system gives as the entropy increase per cycle for the whole specimen an expression similar to equation (2), namely

$$\Delta S = \pi T^{-2} \int \Delta T \, \Delta \mathcal{Q} \, dv \, \Sigma f_k \frac{\nu_k \nu}{\nu_k^2 + \nu^2}. \qquad \ldots\ldots(3)$$

The frequency ν_k is equal to $1/2\pi\tau_k$, where τ_k is the time of relaxation associated with the kth eigenfunction. The weighting factor f_k satisfies the condition

$$\Sigma f_k = 1. \qquad \ldots\ldots(4)$$

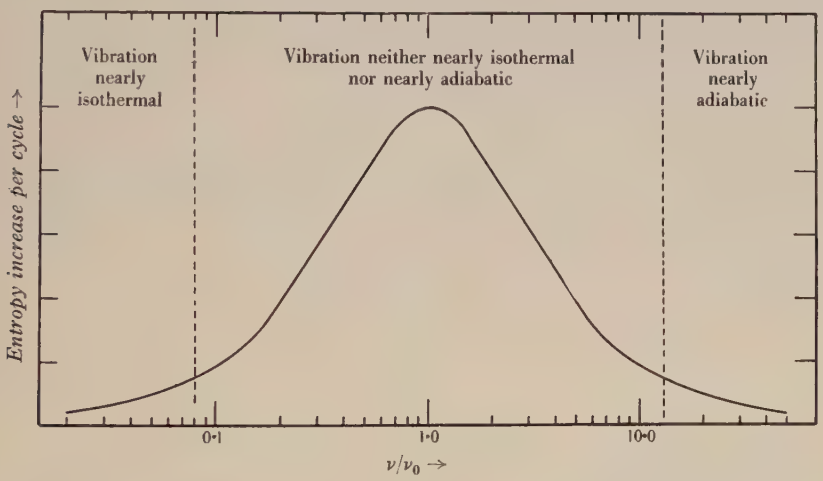

Figure 5. Theoretical dependence of entropy increase per cycle, and of internal friction, with frequency when the thermal diffusion can be described by a single time of relaxation; after Zener[12].

The gain of internal energy per cycle, ΔE, and hence the loss of mechanical energy per cycle, is $T \, \Delta S$. The various measures of internal friction may thus be obtained from equation (1). In particular

$$1/Q = \left\{ \frac{T^{-1} \int \Delta \mathcal{Q} \, \Delta T \, dv}{2 \times \text{energy of vibration}} \right\} \Sigma f_k \frac{\nu_k \nu}{\nu_k^2 + \nu^2}. \qquad \ldots\ldots(5)$$

Both $\Delta \mathcal{Q}$ and ΔT are proportional to the amplitude of vibration, while the energy of vibration is proportional to the square of this amplitude. Hence the internal friction resulting from thermal flow is independent of the amplitude of vibration.

B. *Macroscopic thermal currents*

A pure shear is unaccompanied by any macroscopic thermoelastic effects, as is evidenced by the identity of the adiabatic and isothermal shearing moduli. Hence macroscopic thermal currents are absent in the torsional vibration of cylindrical rods.

On the other hand, pure tensile stresses are associated with comparatively large thermoelastic effects. Pure tensile stresses occur both in longitudinal and in transverse vibrations. In such vibrations the first factor in equation (5) may be reduced by thermodynamics to $(E_S-E_T)/E_S$, where E_S and E_T are the adiabatic and isothermal Young's moduli, respectively. The values of this ratio given in table 1 were calculated from the well-known formula

$$(E_S-E_T)/E_S=TE_T\alpha^2/\rho C_p,$$

where α is the linear thermal expansion coefficient. Since the E_T of a specimen depends not only upon its composition, but also upon its past treatment, this table must be regarded as only approximate.

In both longitudinal and transverse vibrations, all terms in the summation of equation (5) are negligible compared with the first. In these two cases the internal friction thus has the particularly simple form

$$1/Q=\frac{E_S-E_T}{E_S}\,\frac{\nu_0\nu}{\nu_0^2+\nu^2}. \qquad \text{.....(6)}$$

In transverse vibration, the frequency at which the internal friction is a maximum, ν_0, depends upon the shape and dimensions of the cross-section of the specimen. For a rectangular cross-section

$$\nu_0=1{\cdot}57D/(\text{transverse width})^2; \qquad \text{.....(7)}$$

for a circular cross-section

$$\nu_0=2{\cdot}16D/(\text{diameter})^2. \qquad \text{.....(8)}$$

In longitudinal vibrations

$$\nu_0=C^2/2\pi D, \qquad \text{.....(9)}$$

where C is the velocity of wave propagation. Values of the thermal diffusion constant D are given in table 1.

Table 1

Metal	D (in cm²/sec.)	$\frac{E_S-E_T}{E_S}$	Metal	D (in cm²/sec.)	$\frac{E_S-E_T}{E_S}$
Aluminium	0·88	0·0046	Nickel	0·15	0·0029
Antimony	0·12	0·0018	Palladium	0·26	0·0020
Beryllium	0·53	0·0046	Platinum	0·26	0·0015
Bismuth	0·065	0·0014	Rhodium	0·29	0·00069
Cadmium	0·46	0·010	Silver	1·74	0·0034
Copper	1·2	0·0030	Tantalum	0·22	0·00030
Gold	1·1	0·0017	Tin	0·40	0·0040
Iron	0·20	0·0024	Tungsten	0·61	0·00078
Lead	0·24	0·0025	Zinc	0·41	0·0088
Magnesium	0·60	0·0050	Brass (70–30)	0·38	—

Recent experiments have beautifully demonstrated this damping of transverse vibrations by the flow of heat back and forth across the specimen. Bennewitz and Rötger[17] studied the internal friction of wires, about 2 mm. in diameter, of silver, aluminium, brass, steel and glass. Their results are given in figure 6. These experiments were the first to show a maximum in the internal friction when plotted as a

function of frequency. Although cognizant that these maxima were due to a relaxation phenomenon, they were unaware that this pertained to the temperature fluctuation across the specimens. The position of the maxima as calculated by equation (8), shown as vertical lines in figure 6, is in nearly perfect agreement with the observed maxima[14]. On becoming aware of the interpretation of their original experiments, Bennewitz and Rötger then subjected the above theory of damping by thermal currents to a rigorous test by experiments on german silver[18]. This metal was chosen to minimize plastic flow. Their own comparison of this experiment with the theoretical curve is given in figure 7. In constructing the theoretical

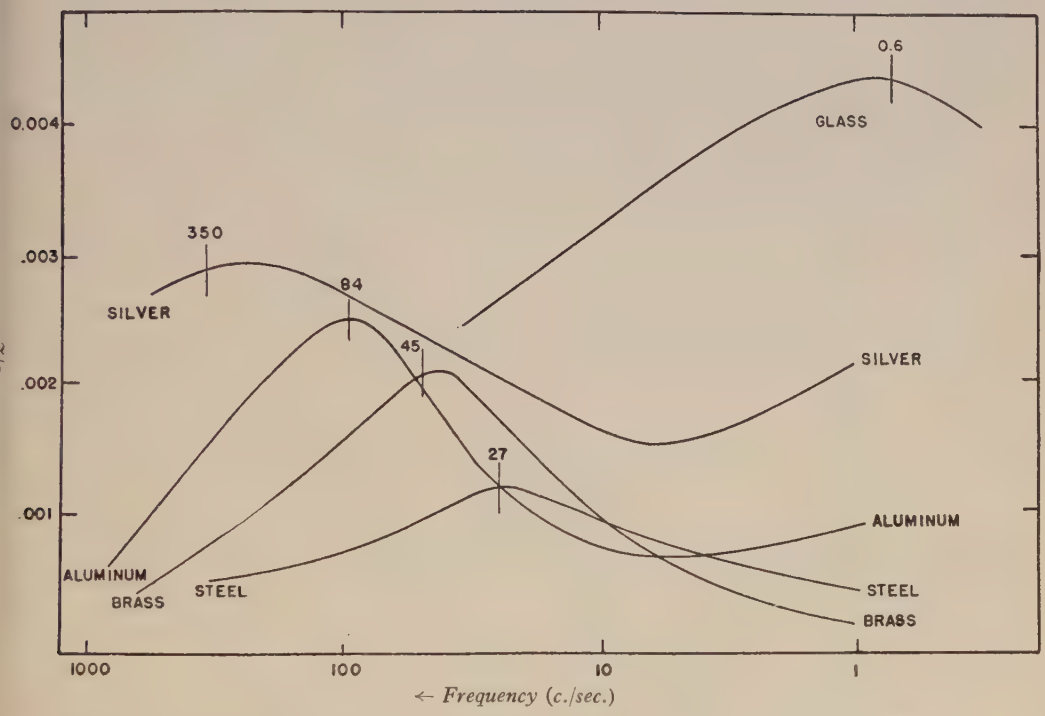

Figure 6. Internal friction of wires vibrating transversely, after Bennewitz and Rötger[17]. Positions of maxima calculated by equation (8) are given by vertical lines.

curve, they computed the ratio $(E_S - E_T)/E_S$ for the actual specimens upon which their internal friction measurements were made.

These experiments, as well as similar ones by the author with Otis and Nuckolls[14] with specimens of rectangular cross-section, indicate that over a wide frequency range the damping of transverse vibrations by thermal currents is of a larger order of magnitude than that due to all other causes.

On the other hand, macroscopic thermal currents from regions of compression to regions of dilatation are unimportant in longitudinal vibrations except for exceedingly high frequencies. Thus for copper, equation (9) gives the frequency for maximum internal friction as $1{\cdot}7 \times 10^{10}$ c./sec. Longitudinal vibrations at ordinary frequencies are nearly adiabatic with respect to such thermal currents.

Contrary to other examples, the vibrations become less adiabatic as the frequency is increased. This is because the relaxation time for temperature equilibrium is proportional to the square of the wave-length, while the period of vibration is proportional only to the first power of the wave-length.

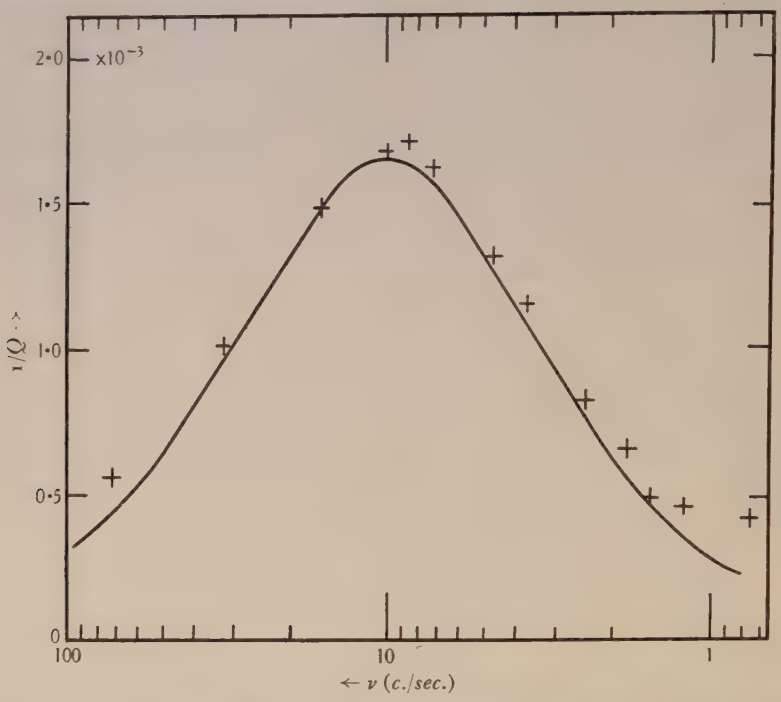

Figure 7. Experimental check of theory of damping of transverse vibrations by thermal currents. Example of german silver, after Bennewitz and Rötger [18]. Curve is given by equation (6) with no arbitrary parameters.

C. *Microscopic thermal currents*

In the previous section we considered the damping by thermal currents arising from stress inhomogeneities inherent in the type of vibration. We now consider the effect of those stress inhomogeneities caused by the deviation of the metal from a perfect single crystal. Of these deviations the polycrystalline nature of a metal is the most striking. The elastic constants of a metal crystal vary markedly with orientation. Examples are given in table 2, column 1, of the ratio of Young's modulus along the [111] direction and along the [100] direction. This elastic anisotropy, together with random orientation, produces microscopic fluctuations in a stress which is macroscopically homogeneous.

The internal friction resulting from the thermal currents between the microscopic stress inhomogeneities is given, at least formally, by equation (5). While an exact calculation of this internal friction is impossible, yet its important features can be obtained from simple considerations [13]. The second factor of Q^{-1} determines the degree of "adiabaticity" of the vibration. This can depend only upon the mean

grain size a of the specimen, its thermal diffusion constant D, and the frequency of measurement ν. The mean grain size is customarily defined by equating a^{-2} to the number of grains visible on a unit surface. Dimensional arguments show that the internal friction can depend upon these three quantities only in the dimensionless product $\nu a^2/D$. When this product is small, the vibration proceeds isothermally, when large it proceeds adiabatically. An estimate of that value of this product for which the internal friction is a maximum may be obtained by replacing the actual temperature fluctuation by one which varies triply periodically with the period $2a$. For such a system $1/\tau = 3D(\pi/a)^2$. Since $1/2\pi\tau$ is the frequency ν_0 at which the internal friction is a maximum, we have the approximate relation

$$\nu_0 a^2/D \simeq 3\pi/2. \qquad \text{.....(10)}$$

The integral of the second factor of Q^{-1} with respect to $\log_e \nu$ is independent of the individual coefficients f_k and ν_k. From the value of this integral, namely π, we are able to calculate the area beneath the curve connecting Q^{-1} and

$$\log_{10}(\nu a^2/D).$$

This is

$$\int_{-\infty}^{\infty} Q^{-1}\, d\log_{10}(\nu a^2/D) = 1{\cdot}364 \left\{\frac{T^{-1}\int \Delta T\, \Delta \mathcal{Q}\, dv}{2 \times \text{energy of vibration}}\right\}. \qquad \text{.....(11)}$$

Rough estimates of this integral have been made[13], and are given in table 2, column 3.

Table 2

Metal	E_{111}/E_{100}*	$10^3 \times \int Q^{-1} d\log_{10}(\nu a^2/D)$ (damping by intercrystallite thermal currents)	$\left(\frac{d\log G}{d\log T}\right)^2$†
Aluminium	1·2	0·025	0·56
Copper	2·8	0·59	0·020
Gold	2·7	0·36	—
Iron (α)	2·1	0·24	0·0081
Lead	3·6	3·0	5·7
Nickel	—	—	0·01
Silver	2·7	0·57	0·060
Tungsten	1·001	0·01	—
Brass (70–30)	3·5	—	—
Brass (β)	8·94	—	—

* All data from E. Schmid and W. Boas, *Kristallplastizität* (Springer, 1935, pp. 200–2), except for lead from reference (36), and for β-brass from reference (34).

† *Handbuch der Experimental Physik*, **5**, 251.

The past experimental literature indicates that, apart from possible macroscopic thermal currents, these intercrystalline thermal currents may be the dominant cause of internal friction at room temperature in annealed polycrystalline non-ferromagnetic metals. According to table 2, aluminium should have the least, lead the greatest, internal friction of the common metals. This is in agreement with experiment. When the product $\nu a^2/D$ is small, the internal friction should increase with an increase in grain size. This has been observed by Förster and Köster[10],

and has been interpreted by them as the cause of the rise of internal friction when the annealing temperature is raised above the recrystallization temperature. Finally, when the product va^2/D is large, the internal friction should decrease with an increase in grain size. In particular, single crystals should have a smaller internal friction than polycrystalline specimens. This has been verified by Read[19].

In order to distinguish the internal friction due to intercrystalline thermal currents from that due to other causes, it is necessary to vary both the grain size and the frequency of measurement. This is now being done in this laboratory by Randall, Rose and the writer[16]. Measurements on longitudinal vibrations have been made at 12,000 and 36,000 c./sec. on specimens of 70–30 brass ranging in

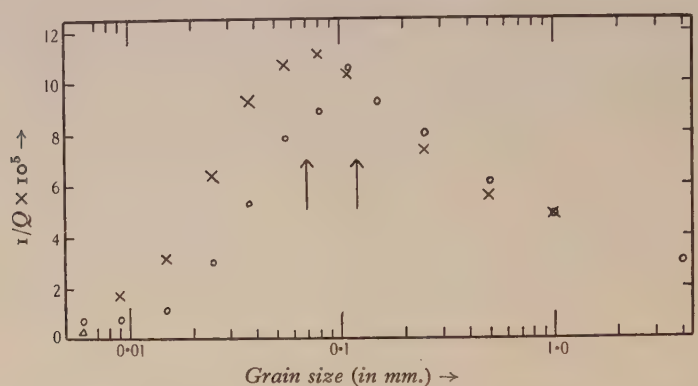

Figure 8. Dependence of internal friction upon grain size. Example of 70–30 brass, after Randall, Rose and Zener[16]. Triangle, measurements at 6000 c./sec. Circles, measurements at 12,000 c./sec. Crosses, measurements at 36,000 c./sec. Vertical lines, positions of maxima as calculated by equation (10).

average grain size a from 0·006 mm. to 4 mm. Our present results are shown in figure 8. The experimental curve for each frequency has a maximum at a grain size very near that given by the theoretical equation (10). If the internal friction is actually a function only of the factor va^2/D, then shifting the points for 36,000 c./sec. to the right (corresponding to an increase of a by a factor of $\sqrt{3}$) should make these points lie upon the 12,000 c./sec. curve. This they nearly do. The slight discrepancy for grain sizes greater than 0·1 mm. may be due to excessive twinning. From the experimental points an estimate may be made of the integral of Q^{-1} with respect to $\log_{10}(va^2)$. This is of the same order of magnitude as, but 20 per cent smaller than, the estimate given in table 2 for copper.

These experiments furnish convincing evidence of the dominating rôle played by intercrystalline thermal currents in the internal friction of metals. In our extreme isothermal case ($va^2/D = 0{\cdot}006$), Q^{-1} is less than $0{\cdot}4 \times 10^{-5}$. For the extreme adiabatic case of a single crystal ($va^2/D \sim \infty$) we must take the upper limit of $1{\cdot}1 \times 10^{-5}$ for copper obtained by Read[19]. In the intermediate range, where the vibration is neither microscopically isothermal nor adiabatic, the internal friction is of the order of 10 times as large, reaching a maximum value of $Q^{-1} = 11 \times 10^{-5}$ at $va^2/D = 4{\cdot}7$. On the other hand, the macroscopic thermal currents accompanying

transverse vibrations give rise to an internal friction larger by still another order of magnitude, reaching a maximum, for brass, of $Q^{-1} = 200 \times 10^{-5}$, as shown in figure 6.

A second way in which actual crystals deviate from perfect single crystals is in the residual stresses introduced by cold working. It has been shown that even in the absence of elastic anisotropy, these residual stresses give rise to thermoelastic damping. The mechanism whereby these thermal currents are generated may be understood by reference to figure 9. Consider two adjacent regions in which the residual shearing stresses are of the opposite sign. If during vibration a uniform shearing stress is superimposed, the total shearing stress of one region will be decreased, that of the other will be increased. The temperature of the first region

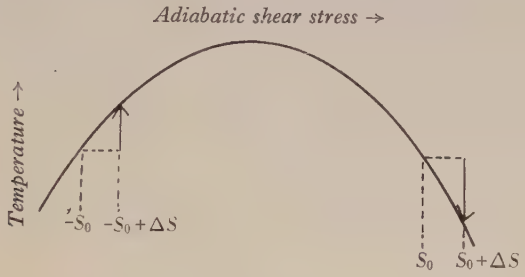

Figure 9. Illustration of thermoelastic damping by residual stresses. Two regions, of shearing stress $-S_0$ and S_0, are subjected to a uniform shearing stress ΔS. The temperature of the first region increases, that of the second decreases.

will be increased, that of the second decreased. The thermal currents resulting therefrom produce an internal friction whose integral with respect to $\log \nu$ is given approximately by[15]

$$\int Q^{-1}\, d \log_{10} \nu \simeq \frac{\Theta}{T}\left(\frac{d \log G}{d \log T}\right)^2.$$

Here the product of Θ and the specific heat per unit volume is the volume density of energy associated with the residual stresses. It may be as large as 5° c. per c.c. for copper, brass, aluminium, and steel[20]. G is the shearing modulus. From the values of $(d \log G/d \log T)^2$ given in table 2, we should expect that, in the appropriate frequency range, the thermoelastic internal friction caused by these residual stresses would be comparable to the internal friction due to other causes. The middle of the frequency scale, on a logarithmic scale, will be near D/L^2, where L is the mean distance between stress inhomogeneities of opposite sign. At present there is no way of estimating this distance.

§ 3. LATTICE DISLOCATIONS AS A SOURCE OF INTERNAL FRICTION

Cold work increases the resistance of a metal to plastic flow, and hence generally reduces the large-amplitude internal friction[21]. On the other hand, it always increases the small-amplitude internal friction, as mentioned in the introduction.

The most striking feature of this cold-work internal friction is its rapid decrease with low-temperature annealing, illustrated in figure 4. The hardening effect of this cold work is not affected by such low-temperature annealing. On the other hand,

the E-modulus is changed considerably by such annealing. At least in steel, the changes of internal friction and of the E-modulus with annealing temperature are closely correlated[10].

The assumption that this correlation is general leads to definite conclusions as to the nature of cold-work internal friction. It at once eliminates the thermoelastic coupling as the primary effect. The calculated difference in the E-modulus for the two extreme cases of microscopically isothermal and microscopically adiabatic vibration is about 100 times smaller than the observed variation of 5 per cent. It rather suggests that the cold working introduces not only lattice distortions, but also lattice imperfections which move under the application of macroscopic stresses, and that it is these imperfections which are removed by low-temperature annealing. Such imperfections are commonly called dislocations[23]. The mobility of these dislocations relaxes the rigidity of the metal, and hence lowers the E-modulus. It is to be expected that their motion will be attended by some hysteresis. Their presence thus endows the metal with internal friction. In contrast to thermoelastic internal friction, this internal friction will be observable even at zero frequency, that is, in static stress-strain tests. It may be this introduction of dislocations which causes the static stress-strain curve of zinc single crystals to acquire a hysteresis loop upon being plastically strained[22].

§ 4. FERROMAGNETISM AS A SOURCE OF INTERNAL FRICTION

The anomalously large internal friction of ferromagnetics has been the subject of numerous experiments[24–30]. The source of this internal friction lies in the magnetoelastic coupling of ferromagnetics. In virtue of this coupling, applied stresses change the magnetization, and, conversely, changes in magnetization induce changes in strain. The magnetization of elementary regions is changed by two methods, (*a*) by rotation of the direction of magnetization, and (*b*) by the movement of the boundary between adjacent regions. The latter type of change is accompanied by hysteresis, and hence contributes to the internal friction. All types of change of magnetization are accompanied by electric eddy currents which tend to oppose the change. The irreversibility of these eddy currents also contributes to the internal friction.

A measure of this magnetoelastic coupling is given by the ratio $(E_S - E_0)/E_S$, where E_S and E_0 are Young's moduli at saturation and at zero magnetization, respectively. This ratio has been extensively investigated[25, 27, 28, 29, 31, 32]. It increases with the magnetic softness of the material. For steel it is less than 10^{-4}, for soft iron about 10^{-3}, for permalloy about 10^{-2}. For hard nickel it is 0·007, for soft nickel 0·1, increasing to a maximum of nearly 0·2 at 200° C. The magnetoelastic coupling vanishes at saturation; here small stresses cannot alter the magnetization.

The motion of the boundaries of the elementary magnetic regions may be compared to the motion of dislocations in non-ferromagnetic metals. This motion gives rise to internal friction even at zero frequency, i.e., it produces a hysteresis loop in the static stress-strain curve. This has been beautifully demonstrated by

Becker and Kornetzki[26] on a soft iron wire. The damping, as well as the area of the static stress-strain loop, was comparatively large when the iron was unmagnetized. When the magnetoelastic coupling was removed by saturating the iron magnetically, both the internal friction and the area of the hysteresis loop were reduced by a large factor.

The damping by eddy currents may be compared to the damping by thermal currents. The diffusion constant for lines of magnetic induction

$$D_B = 10^8/(0{\cdot}4\pi\mu_r\sigma)$$

here plays the same rôle as the thermal diffusion constant D in thermoelastic internal friction. Here μ_r is the reversible permeability, σ is the electrical conductivity in $\text{ohm}^{-1}\,\text{cm}^{-1}$. These eddy currents may likewise be classified as microscopic and macroscopic. The former are due to the at least partial random orientation of the

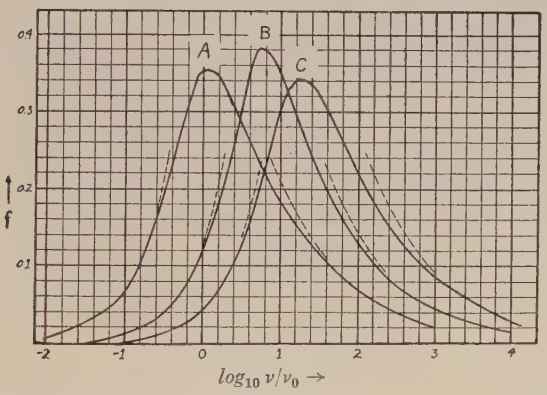

Figure 10. $f(\nu)$ functions associated with macroscopic eddy currents; after Zener[33]. $\nu_0 = D_B/2\pi a^2$. Curve A, transverse vibration of reed, a = transverse width of reed. Curves B and C, longitudinal and transverse vibrations of circular rods, a = radius of rod.

magnetization of the elementary regions. Experiments have not yet been performed to separate the effects of these microscopic eddy currents from the effect of magnetic hysteresis.

The macroscopic eddy currents tend to shield the interior of the specimen from changes of magnetic induction[35]. The internal friction due to these eddy currents is given by[33]

$$Q^{-1} = \frac{E_B - E_H}{E_B} f(\nu).$$

Here E_B and E_H are the Young's moduli at constant B and constant H, respectively. The ratio $(E_B - E_H)/E_B$ may be expressed in terms of directly measurable quantities. The plot of the frequency-dependent function $f(\nu)$ is given in figure 10 for various cases. When $\nu \gg \nu_0$ the average magnetic induction remains nearly constant. When $\nu \ll \nu_0$ the average magnetic field strength remains nearly constant. The internal friction due to these macroscopic eddy currents is appreciable only in the intermediate case $\nu \simeq \nu_0$. It has been separated experimentally from that due to magnetic hysteresis only in one particular case[29].

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X-RAY DIFFRACTION BY FINITE AND IMPERFECT CRYSTAL LATTICES

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ABSTRACT. The Fourier transform of a crystal is a representation which, if fully known, would be equivalent to, and give the same information as, the usual description of a crystal. At the same time the Fourier transform is very closely related to the diffraction properties and it offers the best survey of the diffraction data obtained, and of those missing, for a discussion of crystal shape and of crystal imperfection. The desirability of an exact quantitative x-ray study of the perfection of an individual metal single crystal before and during plastic deformation is urged.

§ 1. FOURIER TRANSFORM AND DIFFRACTED AMPLITUDE

For discussing x-ray diffraction the reciprocal lattice has found general application, but it is not generally realized that the reciprocal lattice is only an incomplete representation of the Fourier transform of the crystal and that much clearness of discussion can be gained by making full use of the conception of the Fourier transform.

If the diffracting body is characterized by the density-distribution of scattering matter $\rho(\mathbf{x})$, the Fourier transform of ρ is the function $F(\mathbf{b})$ in the Fourier integral representation

$$\rho(\mathbf{x}) = \int F(\mathbf{b})\, e^{2\pi i(\mathbf{bx})}\, dv_b; \quad F(\mathbf{b}) = \int \rho(\mathbf{x})\, e^{-2\pi i(\mathbf{bx})}\, dv_x. \qquad \ldots\ldots(1)$$

Here $\mathbf{b}$ is the coordinate vector in Fourier space and dv_b its element of volume. $(\mathbf{bx})$ is the scalar product of the two vectors and since this must be a pure number, in order to make sense in the exponent, $\mathbf{b}$ must have the dimension of the reciprocal of a length, since $\mathbf{x}$ is a length in physical space. Both integrals are to be extended over the whole of their space.

To connect $F(\mathbf{b})$ with diffraction by the crystal, imagine that a plane monochromatic x-ray wave of wave vector $\mathbf{k}_1$ ($|\mathbf{k}_1| = 1/\lambda$) falls on an element dv_x of the body situated at $\mathbf{x}$. Suppose that we observe at great distance the wave scattered classically in an arbitrary direction, thus of wave vector $\mathbf{k}$, where $|\mathbf{k}| = |\mathbf{k}_1|$. Omitting the factor E/r, where E is the amplitude of the incident wave and r the distance of the observer from the crystal, the diffracted wave will have the amplitude $\rho(\mathbf{x})\, dv_x\, e^{2\pi i(\mathbf{k}_1-\mathbf{k},\mathbf{x})}$. Putting $\mathbf{k}-\mathbf{k}_1=\mathbf{b}$ (the dimension of $\mathbf{b}$ is $1/\lambda$), the total amplitude obtained from the body is

$$F(\mathbf{b}) = \int \rho(\mathbf{x})\, e^{-2\pi i(\mathbf{bx})}\, dv_x. \qquad \ldots\ldots(2)$$

For a given direction of incidence $\mathbf{k}_1$, the vector $\mathbf{b}$ connects the origin O of the Fourier space with any point on the sphere of reflection drawn through O with A

as centre, where $OA = -\mathbf{k}_1$. If we intercept all diffracted waves $\mathbf{k}$ proceeding from a given point of propagation A, we obtain a spherical section of the Fourier transform. By observing the effects of a monochromatic wave at all directions of incidence and of diffraction, we can at best explore the region of the Fourier transform of $\rho(\mathbf{x})$ that is included in a sphere of radius $2/\lambda$ surrounding the origin. This is a re-statement of the fact that the resolving power of a radiation of wave-length λ is finite. The more details we wish to obtain concerning $\rho(\mathbf{x})$, the shorter must be the wave-length employed for diffraction. The non-classical Compton scattering, however, sets a limit to the applicability of short wave-length diffraction.

From the quite general formulae (1) we see that the Fourier transform is an equivalent way of representing the crystal, and that it has the advantage of giving nearly all properties of the crystal in a form ready for physical application.† The symmetry of equation (1) with regard to $\rho(\mathbf{x})$ and $F(\mathbf{b})$ furthermore shows that for every result obtained by interpreting $\rho(\mathbf{x})$ as the density in crystal space and $F(\mathbf{b})$ as the diffracted amplitude, a corresponding result may be obtained by interchanging the interpretation of the two spaces and functions.

§ 2. THE PEAK FUNCTIONS AND THE OPERATION OF FOLDING

In order to establish the correspondence for a number of examples, it is convenient to introduce two conceptions. The first is that of a *peak function* of content m, i.e. a function which is zero everywhere except at one point $\mathbf{x}=\mathbf{p}$, where it is infinite to such an order that its integrated value is m. We write this function $Z_p{}^m(\mathbf{x})$; it may be obtained[1] from a Gaussian distribution

$$G_p{}^m(\mathbf{x}) = \frac{m}{(\pi\alpha^2)^{\frac{3}{2}}} e^{-(\mathbf{x}-\mathbf{p})^2/\alpha^2}, \qquad \ldots\ldots(3)$$

by passing to the limit $\alpha \to 0$, or from other suitable functions by a similar process. If we introduce a peak function at every lattice point $\mathbf{x}_l$, we obtain a lattice peak function $\mathbf{z}^m$. This will be the distribution $\rho(\mathbf{x})$ for a simple lattice of point-like atoms of mass m.

The second convenient conception is that of *folding two functions*, e.g. $\rho(\mathbf{x})$ and $\sigma(\mathbf{x})$. Designating by $\widehat{\rho\sigma}$ (*rho fold sigma*) the result of folding the *fold*, we define

$$\widehat{\rho\sigma}(\mathbf{y}) = \int \rho(\mathbf{x})\,\sigma(\mathbf{y}-\mathbf{x})\,dv_x, \qquad \ldots\ldots(4)$$

the integration to extend over all space.

From the theory of Fourier transforms it is known that multiplying and folding are corresponding operations in the two spaces, i.e. folding ρ and σ in crystal space leads to a transform obtained by multiplying the transforms of ρ and σ in Fourier space and vice versa[2].

† No discussion will be given in this paper of the difficulties arising from the fact that, by observing intensities, the absolute values $|F(\mathbf{b})|$ only can be obtained. These difficulties are present also in the study of lattices without imperfections; the Patterson diagram is the direct unamplified presentation of the experimental results (cf. W. L. Bragg, *Nature*, **143**, 73, (1939)). In this paper we shall only deal with ordinary Fourier transforms based on $F(\mathbf{b})$, not on $|F(\mathbf{b})|$.

Let us fold a function $\rho(x)$ into a lattice peak function $\sigma = Z^1$. Since $Z^1(\mathbf{y}-\mathbf{x})$ is zero unless $\mathbf{y}-\mathbf{x}=\mathbf{x}_l$ is a lattice vector, the fold thus reduces to

$$\widehat{\rho Z^1}(\mathbf{y}) = \sum_l \rho(\mathbf{y}-\mathbf{x}_l); \qquad \ldots\ldots(5)$$

that is, by folding with a lattice peak function, $\rho(\mathbf{x})$ is repeated from each lattice point $\mathbf{x}_l$, and, as far as overlapping occurs, the sum is to be taken.

§ 3. STRUCTURE FACTORS

Let us take ρ to be the density due to a single atom or a molecule. The transform of ρ then is the *atomic* or *molecular structure factor* $f(\mathbf{b})$. The transform of a crystal lattice peak function $Z^1(\mathbf{x})$ is the ordinary reciprocal lattice, i.e. a lattice peak function $Z^{1/v_a}(\mathbf{b})$ in Fourier space, giving peaks of content $1/v_a$ at the lattice points $\mathbf{b}_n$. By folding the molecular density distribution into $Z^1(\mathbf{x})$, we obtain the *crystal with extended basis*. On the other hand, the transform will be found by multiplying $Z^{1/v_a}(\mathbf{b})$ into $f(\mathbf{b})$, i.e. the transform is a peak function having peaks of content $\frac{1}{v_a} f(\mathbf{b}_n)$ at the lattice points $\mathbf{b}_n$.

For the study of molecular constitution it is really the molecular structure factor or Fourier transform of the molecule that one tries to extract from X-ray† or electron-diffraction[4] measurements, i.e. one tries to obtain the whole function $f(\mathbf{b})$ from the evidence concerning the values $f(\mathbf{b}_n)$ at the lattice points.

§ 4. THE UNBOUNDED AND THE BOUNDED CRYSTAL

(1) Any perfectly periodic distribution $\rho(\mathbf{x})$ has a lattice peak function as Fourier transform. The fact that $F(\mathbf{b})$ is zero except for the values $\mathbf{b}=\mathbf{b}_n$ implies infinitely high resolving power. A diffracted beam exists only when the sphere of reflection actually passes through a point of the reciprocal lattice. A perfectly periodic distribution is, of course, infinite and unbounded.

(2) Let us call a *regular crystal* a finite part of the perfectly periodic crystal cut out by a closed boundary, without allowing any re-arrangement of the atoms to take place. Mathematically, the density-distribution $\rho_s(\mathbf{x})$ of the finite crystal is obtained by multiplying the distribution $\rho_\infty(\mathbf{x})$ of the perfectly periodic crystal into a *shape function* $s(\mathbf{x})$, which is defined as having value 1 inside and 0 outside the boundary of the finite crystal:

$$\rho_s(\mathbf{x}) = \rho_\infty(\mathbf{x})\, s(\mathbf{x}).$$

The Fourier transform $S(\mathbf{b})$ of the shape function can be interpreted as the diffraction effect of a continuum, of scattering density 1, having the same shape as the crystal. For a prismatic shape function (depending on two coordinates only) the transform will be a two-dimensional function similar to the familiar amplitude-curve of diffraction produced by a light wave behind a diaphragm having the form of the cross-section of the prism.

† The idea of using the structure factor or transform of a single molecule seems to have been first formulated by A. Hettich[3].

The transform of ρ_s is obtained by folding the shape transform into the lattice peak function, representing the transform of ρ_∞. The result will be a function consisting of a repetition of the shape transform round each lattice point $\mathbf{b}_n$. If the regular crystal contains a great number of atoms in all directions, the diffraction effect of the shape will extend only over a small angular range, i.e. it will be narrow as compared to the angular separation of the diffracted beams of different orders, owing to the atomic distances in the crystal. The shape transform does not therefore extend far into the cell of the reciprocal lattice, and practically no overlapping of the shape transforms occurs in consequence of the folding operation (figure 1).

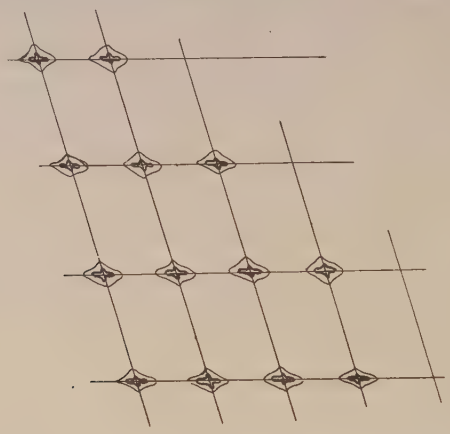

Figure 1. Schematic drawing of Fourier space with the reciprocal lattice of the perfectly periodic crystal and the shape transform surrounding each lattice point.

The shape transform may be regarded as a representation of the resolving power of the crystal due to its finite size and particular shape. If the sphere of reflection passes through sufficiently large values of the shape transform, a diffraction effect will be observed even if the conditions of reflection are not fulfilled for the unlimited lattice.

§ 5. EXAMPLES OF SHAPE TRANSFORMS

Special cases of shape transform are: (*a*) *The crystal flake.* Along the normal to the flake the distribution of the shape transform is the same as that of the diffracted amplitude behind a slit of the same width as the flake, i.e. it is of the form $z^{-1} \sin z$. As a rough approximation the transform can be represented by a little rod normal to the flake, of length $1/Nd$, where N is the number of net planes of spacing d which the flake contains. The length of the rod is thus $1/N$ of the spacing of the points of the reciprocal lattice in the direction normal to the flake. A closer representation should take account of the varying value of the shape transform along the axis of the rod, and of the fact that, for flakes only a few atomic layers thick, the secondary maxima of the shape transforms overlap midway between the nodal points of the reciprocal lattice, so that the transform may reach appreciable values there.

The need for replacing the points of the reciprocal lattice by little rods was first encountered by Kirchner[5] in his discussion of electron diffraction. In metals the x-ray work of Preston[6] on AlCu and of Bradley[7] on FeNiCu has led to the same construction. Guinier[8], in a recent thesis remarkable for the experimental method which it discloses, has investigated the shape factor of the segregated particles in the AlCu system by studying the diffraction in the neighbourhood of the primary monochromatized ray. If the schematic reciprocal lattice shown in figure 1 were correct, there would be no advantage in studying the surroundings of (000) rather than those of any (*hkl*). It should not, however, be overlooked that the atomic structure factor has to be multiplied by the distribution shown in figure 1, and that the intensity of the effect is very much greater near (000) than near any other point.

(*b*) If the crystal is *rod-shaped or needle-shaped*, the shape transform is flat and flake-like. In the plane normal to the axis of the needle the central maximum will be surrounded by secondary maxima of decreasing intensity.

(*c*) The shape transforms of a *sphere* and of a *cylinder* are expressible by Bessel functions, as is well known from diffraction optics. If the particles are very small, the secondary maxima belonging to adjacent lattice points of the reciprocal lattice can overlap midway between the points, and this means that for some directions the regular inner structure enhances the effect due to the smallness of the spherical particle.

If we interchange the meaning of the two spaces, we see that an abrupt falling off of intensities of higher order is to be expected in crystals the molecules of which have a density-distribution falling off in an oscillating manner after the pattern of a Bessel function. Such a distribution may be approximated to by a spherical-shell structure, and this might give an explanation of the sudden decline of intensities with increasing order which has been claimed for some protein molecules.

(*d*) Laue[9] has shown that the shape transform can be easily worked out for *any shape bounded by planes*. A general feature of the transform is that it shows intensity spikes normal to the boundary planes and thus is of a star-like appearance. The familiar diffraction pattern obtained from a rectangular or triangular opening is an example of a shape-star in two dimensions. Laue and Riewe[10] worked out the transform of an octahedron and gave a beautiful interpretation of the electron-diffraction effects observed by Cochrane[11] and by Brück[12] on submicroscopic silver crystals. A similar technique would doubtless make it possible to find the form of minute precipitates at the initial stage of segregation in some alloys.

If there are a great many diffracting crystallites, the definiteness with which the shape transform is manifested depends on the equality of shape, size, and orientation of these crystallites. Homogeneity in both respects should be expected in the case of alloys carefully heat-treated. The homogeneity was remarkable in Cochrane's case of silver films electrolytically deposited on a rock-salt base.

(*e*) As a last example of a Fourier transform, let us consider a lattice formed of Gaussian atoms, i.e. atoms with a distribution of scattering-density according to a

Gaussian function[3]. The transform[1] of a Gaussian of width α is again a Gaussian of width $1/\pi\alpha$:

$$\rho(\mathbf{x}) = \frac{m}{(\pi\alpha^2)^{\frac{3}{2}}} e^{-\mathbf{x}^2/\alpha^2} \rightarrow \mathrm{Trsf}\, f(\mathbf{b}) = m\, e^{-\pi^2\alpha^2\mathbf{b}^2}.$$

It follows that if we build up a lattice of Gaussian atoms by folding ρ into a lattice peak function, the transform is given by the coefficients

$$F_n = \frac{1}{v_a} f(b_n) = \frac{m}{v_a} e^{-\pi^2\alpha^2 b_n^2}.$$

This transformation shows the easiest way of taking into account the influence of temperature movement on the diffraction, by replacing the actual instantaneous position of the atoms by an averaged Gaussian distribution of scattering mass. The transform F_n is then the Debye temperature factor. An anisotropy of the atomic temperature oscillations can easily be taken into account by substituting $(x/\alpha)^2+(y/\beta)^2+(z/\gamma)^2$ for $\mathbf{x}^2/\alpha^2$ in $\rho(\mathbf{x})$, i.e. by substituting an ellipsoidal Gaussian for the spherical Gaussian. The transform $f(\mathbf{b})$ is then a reciprocal ellipsoidal Gaussian. In the case of magnesium, cadmium and similar hexagonal metals, this has been Brindley's[13] procedure to account for the abnormally quick or slow falling away of the intensities of the reflections on the basal plane as compared to the other reflections.

Waller's exact treatment of the influence of heat motion on the diffraction has been discussed in a simplified way by the author[15] by means of the reciprocal lattice, and recently Mauguin and Laval[16] have resumed this study of the Fourier transform from both the theoretical and the experimental sides.

Returning to the simple transform of Gaussians and reversing the significance of the spaces, we obtain a physical interpretation of *Laue's method of discussing the relation between line-width and particle-size*. For this discussion, Laue[17] replaces the true pattern surrounding each lattice point of the reciprocal lattice, i.e. the true shape transform, by a mathematically simple smooth function having the same maximum value and the same width or integral value. The line-width is then obtained by discussing the intersection of these substituted functions with the sphere of reflection. Laue uses two simple functions for the substitution, one being an ellipsoidal Gaussian and the other one an algebraic function:

$$\sigma_1(\mathbf{b}) = e^{-\omega^2(m_1^2 b_1^2+m_2^2 b_2^2+m_3^2 b_3^2)}; \quad \sigma_2(\mathbf{b}) = \frac{\text{const.}}{\{1+\omega^2(m_1^2 b_1^2+m_2^2 b_2^2+m_3^2 b_3^2)\}^2}.$$

Both shape transforms do not extend far from the lattice points $\mathbf{b}_n$. The shape of the crystal corresponding to $\sigma_1(\mathbf{b})$ is an ellipsoidal Gaussian again, with half-width covering a great many cells. The smoothing out of the true shape transform in Laue's discussion is thus equivalent to substituting for the true, sharply bounded, particle an average one in which the masses fall off exponentially with the square of the distance from the centre. The function $\sigma_2(\mathbf{b})$ is the shape transform for a crystal of similar mass distribution, differing only in that the decay of the masses is exponentially proportional to the first power of the distance from the centre.

It is easy to understand that in either way an expression can be given to the average size and shape of the particles but also that these will cease to be appropriate if we have to deal with a distribution around a standard uniform size rather than with one ranging down to zero size.

(*f*) The shape transform $S(\mathbf{b})$ is always centro-symmetrical in the sense that $S(-\mathbf{b}) = S^*(\mathbf{b})$, where the * denotes the complex conjugate value. This follows from equations (1) for every real function of $\mathbf{x}$. By the folding operation of $S(\mathbf{b})$ into the lattice peak function, the resulting Fourier transform of the finite regular crystal will be centrosymmetrical about each lattice point. If, therefore, acentric distributions are found experimentally, these cannot be explained by particle-size or crystal-shape. Such is the case in Mr Preston's[6] beautiful work on aluminium-copper alloys where monochromatic streaks were obtained streaming out from normal reflection spots on one side only. This could be interpreted in the reciprocal lattice by making the lattice points the corner points of little cube-edges directed away from the origin. Any shape effect could only result in replacing the point by a centrosymmetrical set of lines.

§ 6. SOME REMARKS ON THE EXPERIMENTAL STUDY OF SHAPE TRANSFORMS

There are two points I would like to emphasize regarding the study of shape transforms. The first is that the shape transform can be studied equally in any order of diffraction, since it is the same round each point of the reciprocal lattice. In order to obtain a complete survey one has to produce reflections of the same order under varying incidence, so as to obtain a variety of intersections of the shape transform with the sphere of reflection. Evidently data obtained on different orders can also be combined into one picture provided it has been established that the diffuseness of the reciprocal lattice is due to a shape factor. The surroundings of the primary beam (000) have the special advantage of higher intensity due to the atomic factor. It is necessary to use monochromatized rays in order to obtain a clear background near the primary beam. Guinier[8] has done this without sacrifice of intensity, by using a focusing bent-crystal monochromatizer. The aperture of this must, however, be kept small compared to the angular width of the shape transform for the wave-length employed.

The second point is the desirability of studying the shape transform in single-crystal photographs, after the manner of Preston, Guinier, and others. X-ray micro methods, such as those developed by Kratky[18] to obtain diagrams from regions of a crystal 1/100 mm. wide, should prove of great value in preventing the blurring which is bound to occur as a result of the superposition of shape transforms from crystallites varying in size and orientation.

It would lead us too far to discuss the representation of deformed lattices by the Fourier transform. The methods discussed above allow one, for example, to obtain directly the essential properties of the curves given recently by Kochendörfer[19] for the diffraction on a lattice with a sinusoidal displacement of the

reflecting planes. But I would like to stress the importance of making a close X-ray study of the reflecting power of a single metal crystal before and after plastic deformation, in order to ascertain the size and perfection of the coherent domains in the crystal. The reflecting power of a crystal of the mosaic type is many times that of a perfect crystal, and it has been shown by Renninger[20] that in a crystal such as rock salt both types of curves can be realized to within about 5 per cent, on the same material, according to treatment. The measurement of the integrated reflection allows one to determine the size of the coherent domains, while the study of the angular distribution of the reflected radiation shows the angular spread of the orientation of these domains. If a small proportion of a metal single crystal was picked out as being approximately perfect with regard to its X-ray diffraction, this would give a much more definite starting point for an X-ray study of the initial stages of plastic deformation than the unspecified material which has been used for this purpose up to the present. Although an investigation of the type of those carried out by Allison[21] and by Parratt[22] on calcite and by Renninger on rock salt is laborious, it should be worth while performing it on a metal crystal in view of the importance of obtaining as accurate data as possible on the fundamental process of gliding.

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Note added in proof. The latest issue of the *Physical Review* contains two papers by A. L. Patterson[23] which cover partly the same ground as this paper. The shape transforms for several regular shapes, not dealt with before, can be found there.

DISCUSSION. PART IV

Dr E. C. Stoner. Those present who are interested in magnetism no doubt hoped that information would be forthcoming from the mechanical side enabling more definite conclusions to be drawn about the character of internal strains in metals. They have, however, been left with considerable freedom to invent strains of a kind which seem most suitable for magnetic purposes. The work of Becker, Preisach, Kersten and others on the relations between magnetization and strain has been of immense value in introducing order into a wide range of previously disordered magnetic phenomena. None the less, it should be made clear that the treatment is as yet at a very qualitative stage. The main quantities entering into the treatment are the magnetostriction λ, the interchange interaction energy A per unit volume, and the internal strain σ_i. Attempts to calculate λ on a purely theoretical basis have hitherto been far from successful, but for the actual applications it is sufficient to know the experimental values. When λ is of the same sign for different crystal directions, as for nickel, a mean value may be used in a fairly straightforward way. It would be much more troublesome to work out the effect of a different sign for different directions, as for iron, where λ_{100} is positive and λ_{111} negative, so that it is not merely lack of experimental data for single crystals which holds up a quantitative treatment of some of the alloys of particular magnetic interest. Little more than the order of magnitude of A has been calculated in a purely theoretical manner; and the estimate of its value from the Curie temperature in the usual way may well be in error by 50 per cent. As to σ_i, it must be remembered that internal stresses, to be magnetically effective, must be of the nature of longitudinal tensions or compressions (rather than of the nature of a hydrostatic pressure) and it is not easy to see how stresses of the required kind can arise in a metal. As pointed out by Becker, the symbol σ_i has not precisely the same significance in the different formulae, and the choice as to whether 90° or 180° walls are to be considered seems to be made without much reference to implications about the frequency-distribution of the different types of boundary in the material. In spite of these imperfections, the theoretical treatment does provide a most useful way of thinking about the various magnetic processes, and of finding interrelations between them.

It is mainly strain irregularities which have been considered, and, although these are undoubtedly primarily determinative of the general character of the magnetization curves in some cases, it may be doubted whether the strain effects are of predominant importance as universally as is sometimes supposed. The demagnetization energy as dependent on domain shape has been considered in some connexions, but its large magnitude is seldom appreciated. For an elongated domain, the difference in energy density for magnetization along and at right angles to the length is of the order $2\pi I^2$, say 10^7 for $I = 10^3$; this is much greater than the crystal-anisotropy energy differences, of the order 10^5, and, even for nickel, would correspond

to magneto-strain energy differences for strains of the order 10^3 kg./mm.^{2} It seems clear that much more detailed consideration must be given to domain shape effects in dealing with the general problem of domain boundary distribution.

Coercivity depends essentially on the maximum gradient of domain boundary energy $(\partial\gamma/\partial x)_{\max}$, γ being proportional to $\sqrt{(A\lambda\sigma)}$; see Becker's equation (8). In the Becker treatment it is the effect of fluctuations of σ which has been considered. Although there may be large strains in those alloy systems in which high coercive forces are developed, it would seem that here fluctuations in the A factor are likely to be of much greater direct importance. The picture of the course of the segregating process to which Bradley has been led from the x-ray analysis of the Fe-Ni-Al magnet alloys seems immediately compatible with the type of interchange interaction variation which would be required to account for high coercivity; this could hardly be explained, without considerable forcing, in terms of the actual associated strain fluctuations which would be expected to occur. Formally, much of the Becker treatment could be taken over, though the physical interpretation would be different. That something other than fluctuations of strain is required is suggested by the fact that in these alloys the coercivities obtained are larger by a factor of the order 10 than those of the older magnet steels. Ordinarily, fluctuations of both strain and interchange energy will occur, and it is a question of which is the more important magnetically. In the limiting case, the interchange effect may be so much the more important that the primary factor to be considered is simply that of local variation of composition; and the problem arising is then that of linking up the magnetic properties with the state of segregation, about which knowledge is rapidly being gained.

Dr F. Preisach. In order to investigate experimentally the theory of coercive force discussed by Prof. Becker, it would be desirable to vary the distribution of internal strains, without changing their average value. However, there seems to be no known method of causing such a variation of internal structure. A suitable method of studying the influence of a treatment affecting both the average value and the distribution of internal strains is to consider the variations of the coefficient p_c, defined in formula (17) of Prof. Becker's paper. This quantity is likely to characterize the geometry of distribution of the strains. I made an attempt therefore to study the magnetic properties of an age-hardening alloy, by observing not only the coercive force during ageing, but, simultaneously, the initial permeability also, in order to calculate the quantity p_{σ_i}. The composition of the alloy chosen (55 per cent Ni, 45 per cent Fe with an addition of 0·5 per cent by weight of Be) was such that the saturation and the Curie temperature were not appreciably affected during precipitation[1].

I found as a common feature of all the three quantities of importance—σ_i (inversely proportional to the initial permeability), H_c, and p_c (proportional to the ratio H_c/σ_i)—that their plots against ageing-time have a maximum value after which a decrease with continued ageing takes place. The curves are shifted in such a manner that p_c reaches the maximum first, σ_i last. At the time when the measurements were

made, neither theory nor experience about age hardening was as far developed as it is at present. Thus, at this time I only emphasized the fact that p_c increases approximately simultaneously with H_c. Consequently, magnetic age-hardening is probably caused by a variation of structure which influences at the same time not only the average value, but also the distribution of internal strains. My hypothesis that the decrease of magnetic hardening during the second period of ageing is due to the commencement of a plastic flow was put forward by J. L. Snoek and W. G. Burgers[2]. In agreement with this assumption, they observed that a broadening of the x-ray lines begins in the second period of ageing, during the decrease of coercive force. At present I should like to draw attention to the fact that p_c is already decreasing during the period in which σ_i is still increasing. As an explanation I would suggest that in a period when stresses due to precipitation are still increasing, the precipitated particles begin to grow and agglomerate—a phenomenon accounted for by observations made by Dr Sykes on different age-hardening alloys. In consequence, we have to consider a corresponding growth in the size of homogeneously strained domains of the matrix crystal. The decrease of p_c may consequently be interpreted as due to an increase in the distance l, discussed by Prof. Becker and representing an average diameter of homogeneously strained domains. It is not clear, however, how we are to explain the first period of ageing, when p_c is increasing. A first and most simple explanation, assuming a monotonic increase of l with time, is that precipitation begins with finely dispersed particles, the average distance apart of which is smaller than the thickness of Bloch's boundary (in our alloy roughly 300 atomic distances). With agglomeration of precipitated particles their average separation increases, and the distance l attains and surpasses the thickness δ. In other words the curve of figure 5 in Prof. Becker's paper could be translated into a plot of p_c against time. A second possible assumption in connexion with these ideas seems, however, to be more probable. Supposing that at the beginning of precipitation there are only a few particles which will affect the magnetic properties, then their average distance is large. As the number of particles increases, their average distance decreases to a minimum, which may attain a value comparable with the thickness of the boundary δ. With the beginning of the growth of particles during the second period we have an increase of the average distance already considered. There is obviously a possibility, according to this picture, of obtaining two maxima of p_c, if the minimum value of l is less than that of δ.

In discussing coercive force in age-hardening alloys, we must take into detailed consideration the discovery of Mr Preston and Dr Bradley, which was discussed during this conference, that the segregation occurs sometimes—perhaps often—in the form of plates of considerable extension. If we assume that in the interior of a ferromagnetic crystal surfaces of unmagnetic atoms, having a thickness of several atomic distances, are created, then this phenomenon is likely to become important in the discussion of the surface energy of Bloch's boundary. In this case the constant A, which measures the exchange energy—see formula (8) of Prof. Becker's paper—is subjected to drastic local changes, and the surface of a precipitated plate becomes a natural stable seat for Bloch's boundary. However, the maximum value

of p_c accounted for by this process will not exceed the theoretical limit given by Prof. Becker. The variation of p_c with ageing can probably be interpreted on similar lines to those mentioned above, by considering an average distance of segregated lamellae.

Finally, I should like to emphasize the importance of studying magnetic age-hardening in specimens which can be treated so as to give rectangular hysteresis loops, in order to observe the variations of the limiting field H_0. This method would probably permit a choice between different possible interpretations. Further data available from these experiments are provided through the determination of the starting field in connexion with the properties of the natural nuclei of reversed magnetization. The study of this quantity is likely to give additional information concerning the variation of internal structure.

Dr W. G. Burgers. With regard to Prof. Ewald's paper; an optical model which may be useful in visualizing some geometrical features of electron-diffraction photographs, as deduced by means of the reciprocal lattice, is described in *Z. Kristallogr.* **95**, 54 (1936).

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